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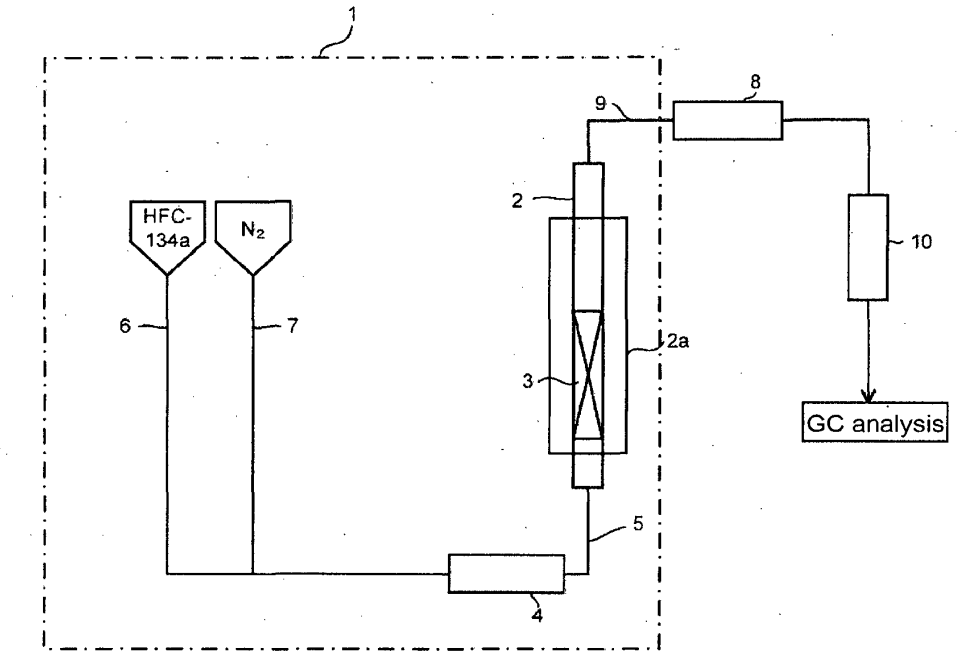
(54) METHOD FOR PRODUCING TRIFLUOROETHYLENE

(57) To produce trifluoroethylene stably with a high selectivity by reacting 1,1,1,2-tetrafluoroethane with a solid reactant efficiently while formation of by-products such as polymer carbon is suppressed.

A material gas containing 1,1,1,2-tetrafluoroethane is made to flow through a layer consisting of a particulate solid reactant having an average particle size of from 1 μm to 5,000 μm to bring the solid reactant and 1,1,1,2-tetrafluoroethane into contact with each other in a state where the layer consisting of the solid reactant is fluidized.

Fig. 1



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Description

TECHNICAL FIELD

[0001] The present invention relates to a method for producing trifluoroethylene, more particularly, a method for efficiently producing trifluoroethylene from 1,1,1,2-tetrafluoroethane.

BACKGROUND ART

[0002] Trifluoroethylene (HFO-1123), which has a low global warming potential (GWP), is greatly expected in recent years as a new refrigerant which may replace difluoromethane (HFC-32) and 1,1,1,2,2-pentafluoroethane (HFC-125) which are greenhouse gases.

[0003] In this specification, abbreviated names (e.g. refrigerant numbers) of halogenated hydrocarbon compounds are described in brackets after the compound names. As the case requires, the abbreviated names are employed instead of the compound names.

[0004] Heretofore, a method for producing HFO-1123 from 1,1,1,2-tetrafluoroethane (HFC-134a) which is a relatively inexpensive material has been known. For example, Patent Document 1 discloses a method of subjecting HFC-134a to dehydrofluorination in a gaseous phase using a metal fluoride as a catalyst. Further, Patent Document 2 discloses a method of reacting HFC-134a with a metal hydroxide such as calcium hydroxide in a gaseous phase.

[0005] However, either of the methods disclosed in Patent Documents 1 and 2 has the following problems since HFC-134a in a gaseous phase is brought into contact with and reacted with a solid reactant forming a fixed bed.

(1) Since it is difficult to uniformly mix particles of the solid reactant with HFC-134a and bring them into contact with each other, the degree of conversion of the solid reactant is low. Further, since the reactivity in the reaction of forming HFO-1123 from HFC-134a is low, it is necessary to bring HFC-134a into contact with the solid reactant for a long period of time.

(2) Since the heat removal efficiency is poor when a fixed bed is used, hot spots are likely to form. Accordingly, side reactions such as cleavage of a carbon-carbon bond of HFC-134a are likely to occur, and by-products such as low molecular weight hydrocarbon compounds such as methane, ethylene and propylene and polymer carbon (graphite) are likely to form.

(3) Since the amount of by-products such as polymer carbon is large, the polymer carbon is attached to the surface of the solid reactant, whereby the degree of conversion of HFC-134a is remarkably lowered with time. Thus, stable production of HFO-1123 is difficult.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0006]

Patent Document 1: JP-A-2010-533151
Patent Document 2: WO2011/157907

DISCLOSURE OF INVENTION

TECHNICAL PROBLEM

[0007] The present invention has been made to solve the above problems, and its object is to provide a method for producing HFO-1123 stably with a high selectivity, by efficiently reacting HFC-134a which is an inexpensive material with a solid reactant, while formation of by-products such as low molecular weight hydrocarbon compounds and polymer carbon is suppressed.

SOLUTION TO PROBLEM

[0008] The method for producing HFO-1123 of the present invention comprises making a material gas containing HFC-134a to flow through a layer consisting of a particulate solid reactant having an average particle size of from 1 μm to 5,000 μm to bring the solid reactant and HFC-134a into contact with each other in a state where the layer consisting of the solid reactant is fluidized.

[0009] In the present invention, "in a state where the layer consisting of a solid reactant (hereinafter sometimes referred to as a solid reactant layer) is fluidized" is a state created by extruding a fluid such as a material gas upward (in a direction opposite to the direction of gravitational force) and is a state in which particles of the solid reactant are suspended and floating in the fluid. The upward drag by a fluid flow, the gravity and the buoyancy acting on the solid particles are balanced, and the entire solid reactant layer behaves as a uniform fluid. On that occasion, the pressure loss when the fluid passes through the solid reactant layer is equal to a difference between the gravity and the buoyancy, and so long as a fluidized state is maintained, the pressure loss of the solid reactant layer is always constant at a difference between the gravity and the buoyancy even when the flow velocity of the fluid is changed. A solid reactant layer in such a fluidized state will be referred to as a fluid bed or a fluidized bed.

[0010] In a case where the solid reactant layer is "in a fluidized state", particles of the solid reactant constituting the layer float and flow in the fluid, and thus the term "fluidized state" refers to both the solid reactant layer and the particles of the solid reactant.

ADVANTAGEOUS EFFECTS OF INVENTION

[0011] According to the present invention, in production of HFO-1123 from HFC-134a, sufficiently high degree of conversion of 134a and selectivity for HFO-1123 are achieved and in addition, formation of hot spots in the reaction site can be prevented, and formation of by-products such as low molecular weight hydrocarbon compounds and polymer carbon can be suppressed, whereby HFO-1123 can be obtained efficiently and stably.

[0012] Further, the production method of the present invention has an advantage over a method of bringing HFC-134a in a gaseous phase into contact with a solid reactant in a fixed bed and reacting them, as follows.

[0013] That is, by the reaction in the fluidized bed, the efficiency of removal of the heat of reaction is high and hot spots are less likely to form, and thus progress of side reaction (cleavage of carbon-carbon bond) of HFC-134a can be suppressed. Accordingly, low molecular weight hydrocarbon compounds and polymer carbon (graphite) are less likely to form as by-products, and the selectivity for the reaction for formation of R-1123 tends to improve. Further, since polymer carbon is less likely to form as a by-product, a decrease in the degree of conversion of HFC-134a with time caused by attachment of the polymer carbon to the surface of the solid reactor tends to be prevented, and R-1123 will be stably obtained.

[0014] And, HFO-1123 obtained by the production method of the present invention is useful as a refrigerant which replaces HFC-32 and HFC-125 which are greenhouse gases, and as a material monomer and a synthetic intermediate of a functional material such as a piezoelectric element or a film.

[0015] As described above, according to the production method of the present invention, it is possible to produce HFO-1123 useful as a new refrigerant and as a material monomer or a synthetic intermediate of a functional material, from HFC-134a as a material, by an efficient method with a high degree of conversion of HFC-134a and a high selectivity for HFO-1123, and with small loss due to formation of impurities. Further, since side reactions such as cleavage of a carbon-carbon bond of HFC-134a can be suppressed and polymer carbon is less likely to form as a by-product, a decrease in the degree of conversion of HFC-134a with time can be prevented, and HFO-1123 can be produced stably over a long period of time.

BRIEF DESCRIPTION OF DRAWINGS

[0016]

Fig. 1 is a drawing illustrating an example of a fluidized bed reaction apparatus used in the production method of the present invention.

Fig. 2 is a diagram illustrating a fluidized bed reaction apparatus provided with a differential pressure measuring device used in Examples of the present invention.

Fig. 3 is a drawing illustrating a fluidization visualized test apparatus provided with a differential pressure measuring device used in Examples of the present invention.

Fig. 4 is a graph obtained by plotting a differential pressure relative to a linear velocity of a nitrogen gas in Fluidization Example 1.

Fig. 5 is a graph obtained by plotting a differential pressure relative to a linear velocity of a gas mixture of HFC-134a and nitrogen in Fluidization Example 2.

Fig. 6 is a graph obtained by plotting a differential pressure relative to a linear velocity of a nitrogen gas in Fluidization Example 3.

Fig. 7 is a graph obtained by plotting a differential pressure relative to a linear velocity of a gas mixture of HFC-134a and nitrogen in Fluidization Example 4.

Fig. 8 is a graph obtained by plotting a differential pressure relative to a linear velocity of a nitrogen gas in Fluidization

Example 5.

Fig. 9 is a graph obtained by plotting a differential pressure relative to a linear velocity of a nitrogen gas in Fluidization Example 6.

Fig. 10 is a graph obtained by plotting a differential pressure relative to a linear velocity of a nitrogen gas in Fluidization Example 7.

Fig. 11 is a graph obtained by plotting a differential pressure relative to a linear velocity of a nitrogen gas in Comparative Fluidization Example 1.

Fig. 12 is a graph obtained by plotting a differential pressure relative to a linear velocity of a nitrogen gas in Comparative Fluidization Example 2.

Fig. 13 is a graph obtained by plotting a differential pressure relative to a linear velocity of a nitrogen gas in Comparative Fluidization Example 3.

Fig. 14 is a graph obtained by plotting a differential pressure relative to a linear velocity of a nitrogen gas in Comparative Fluidization Example 4.

Fig. 15 is a graph obtained by plotting a differential pressure relative to a linear velocity of a nitrogen gas in Comparative Fluidization Example 5.

Fig. 16 is a diagram illustrating a fluidized bed reaction apparatus provided with a differential pressure measuring device used in Examples of the present invention.

Fig. 17 is a graph obtained by plotting a differential pressure relative to a linear velocity of a nitrogen gas in Fluidization Example 8.

Fig. 18 is a graph obtained by plotting a differential pressure relative to a linear velocity of a nitrogen gas in Fluidization Example 9.

Fig. 19 is a graph obtained by plotting a differential pressure relative to a linear velocity of HFC-134a in Fluidization Example 10.

Fig. 20 is a graph obtained by plotting a differential pressure relative to a linear velocity of a nitrogen gas in Fluidization Example 11.

Fig. 21 is a graph obtained by plotting a differential pressure relative to a linear velocity of a nitrogen gas in Fluidization Example 12.

DESCRIPTION OF EMBODIMENTS

[0017] Now, an embodiment of the present invention will be described. The present invention is by no means restricted to the following embodiment.

[0018] The production method according to an embodiment of the present invention comprises making a material gas containing HFC-134a to flow through a layer consisting of a particulate solid reactant having an average particle size of from 1 μm to 5,000 μm, to fluidize the layer consisting of the solid reactant, thereby to bring particles of the solid reactant in a fluidized state and HFC-134a into contact with each other, whereby dehydrofluorination of HFC-134a is made to progress and HFO-1123 is produced. Such a reaction of the solid reactant in a fluidized state and HFC-134a by contact is carried out by using a fluidized bed reaction apparatus which has a fluid bed (fluidized bed) consisting of the solid reactant formed in a reactor.

[0019] The reaction of HFC-134a with the solid reactant in the production method of the present invention may be represented by the following reaction formula (1) or (2) as a representative example. The reaction formula (1) represents a reaction in a case where the solid reactant functions as a catalyst (Cat.), and the reaction formula (2) represents a reaction in a case where the solid reactant functions as a basic reactant (MOH: M represents a metal).

$$CF_3\text{-}CH_2F + \text{solid reactant (Cat.)} \rightarrow CF_2{=}CHF + HF \qquad (1)$$

$$CF_3\text{-}CH_2F + \text{solid reactant (MOH)} \rightarrow CF_2{=}CHF + MF + H_2O \qquad (2)$$

When HFC-134a is brought into contact with the solid reactant, dehydrofluorination reaction occurs in which one of fluorine atoms bonded to a carbon atom to which three fluorine atoms are bonded between the two carbon atoms of HFC-134a, and one of hydrogen atoms bonded to the other carbon atom, leave simultaneously. And, by such dehydrofluorination reaction of HFC-134a, HFO-1123 forms. On that occasion, the fluorine atom and the hydrogen atom which have left form hydrogen fluoride when the solid reactant functions as a catalyst, and form a metal fluoride (MF) and water simultaneously when the solid reactant functions as a basic reactant.

[0020] According to the production method of the present invention, by contact of HFC-134a with the solid reactant, HFC-134a is brought into contact with the particulate solid reactant having an average particle size of from 1 μm to 5,000 μm which forms a fluidized bed and is in a fluidized state, whereby HFC-134a is reacted with a sufficiently high degree of conversion, and HFO-1123 can be obtained with a high selectivity.

(Fluidized bed reaction apparatus)

[0021] As a reaction apparatus in the embodiment of the present invention, a fluidized bed reaction apparatus is employed. As the fluidized bed type reaction apparatus, a fluid bed type reaction apparatus or a riser type reaction apparatus may be employed. With a view to stably producing HFO-1123 efficiently, a fluid bed type reaction apparatus is preferred.

[0022] A fluid bed type reaction apparatus comprises, for example, a reactor (hereinafter sometimes referred to as a fluidized bed reactor) in which a fluid bed (fluidized bed) is formed and as the case requires, in the interior of the reactor, a cooling coil for heat removal or an electric heater to heat the interior. Further, it has a cyclone which separates the material gas or the reaction gas from the solid reactant on the upper portion in the interior of the reactor. The cyclone may be disposed on the outside of the reactor. Further, it has a gas dispersing apparatus to supply a material gas at the bottom and/or at the lower portion of the reactor. As the material of the reactor, glass, iron, nickel, or an alloy containing iron or nickel as the main component may, for example, be used.

[0023] In the production method of the present invention, each of supply of the material gas containing HFC-134a and supply of the solid reactant to the fluidized bed reactor may be carried out continuously, or only supply of the material gas containing HFC-134a may be carried out continuously, and the solid reactant is supplied by the batch. Now, the method of the present invention will be described with reference to a case where only the material gas containing HFC-134a is continuously supplied, and the solid reactant is supplied to the fluidized bed reactor by the batch, however, the present invention is by no means restricted thereto.

(Material gas containing HFC-134a)

[0024] The material gas containing HFC-134a used in the present invention is present always in a gaseous phase under the after-mentioned reaction conditions. HFC-134a may be HFC-134a with a purity of 100% (mol%), or may be one containing 1,1,2,2-tetrafluoroethane (HFC-134) which is an impurity derived from the production method. In a case where it contains HFC-134a, the purity of HFC-134a is preferably at least 50 mol%. That is, the material gas may be one containing HFC-134a with a purity of 100% (mol%) or may be one containing HFC-134a with a purity of 50 mol% containing impurities such as HFC-134.

[0025] From the viewpoint of suppression of side reaction and stable progress of fluidized bed reaction, the material gas preferably contains, in addition to HFC-134a with a purity of at least 50 mol%, an inert gas such as nitrogen, argon or helium. By such a gas, HFC-134a as a reaction component can be diluted. Hereinafter such a gas will be referred to as a diluent gas. Further, incorporation of such a diluent gas is preferred also from the viewpoint of easiness of supply of HFC-134a to the reactor and adjustment of the flow rate.

[0026] In a case where the material gas contains a diluent gas, the content of the diluent gas is preferably at most 95 mol%, particularly preferably at most 50 mol% based on the entire amount of the material gas containing HFC-134a, in view of the reaction efficiency, suppression of side reaction, etc. Further, the content of HFC-134a based on the entire amount of the material gas is preferably at least 5 mol% and less than 100 mol%, particularly preferably at least 50 mol% and less than 100 mol%.

[0027] In an embodiment in which the material gas containing HFC-134a and the solid reactant are continuously brought into contact with each other and reacted, by controlling the flow rates of the respective components (HFC-134a and the diluent gas) constituting the material gas per unit time, the molar ratio of the respective components in the material gas can be controlled.

(Solid reactant)

[0028] The solid reactant used in the present invention is a particulate solid reactant having an average particle size of from 1 μm to 5,000 μm. In this specification, the average particle size is a value measured by a laser diffraction/scattering particle size analyzer.

[0029] If the average particle size of the solid reactant is less than 1 μm, adhesion property of particles tends to be high, and when the material gas containing HFC-134a is made to flow through and is brought into contact with the solid reactant layer, the solid reactant layer is less likely to be fluidized, whereby uniform mixing and contact of the particles of the solid reactant with HFC-134a tend to be difficult, and the degree of conversion of HFC-134a tends to be low. Further, the heat removal efficiency in the solid reactant layer as the reaction site tends to be low, and hot spots are likely to form, whereby side reactions such as carbonization are likely to occur, and due to adhesion of a carbon compound, the degree of conversion of HFC-134a will be decreased with time. On the other hand, if the average particle size of the solid reactant exceeds 5,000 μm, the velocity of flow of the material gas necessary to fluidize the particles of the solid reactant tends to be too high. Accordingly, in order to secure a sufficient contact time for the reaction with HFC-134a, a large-sized reactor is necessary, and the production efficiency tends to be low.

[0030] As mentioned above, if the average particle size of the solid reactant is out of the range of from 1 μm to 5,000 μm, even if HFC-134a is made to flow through the solid reactant layer, it tends to be difficult to fluidize the solid reactant layer sufficiently to secure uniform contact with HFC-134a. Thus, it tends to be difficult to achieve a sufficiently high degree of conversion of HFC-134a thereby to stably produce HFO-1123 with a high selectivity. The average particle size of the solid reactant is preferably within a range of from 40 μm to 5,000 μm, more preferably from 40 μm to 500 μm.

[0031] Here, the fluidized state of the solid reactant layer may be examined, for example, by (a) visual observation or by (b) measuring a differential pressure.

(a) Visual observation

[0032] Whether the upper portion and the lower portion of the solid reactant layer are mixed is visually observed, and the fluidized state is evaluated on the basis of the following standards.

Completely fluidized state: The upper portion and the lower portion are mixed in the entire solid reactant layer.
Partially fluidized state: The upper portion and the lower portion are mixed in a part of the solid reactant layer.
Non-fluidized state: The upper portion and the lower portion of the solid reactant layer are not mixed.

(b) Measuring differential pressure

[0033] A difference in the gas pressure between on the inlet side and on the outlet side of a reactor (hereinafter referred to as a differential pressure) is measured. And, a graph is prepared by plotting the differential pressure relative to the velocity of flow (for example, the after-mentioned linear velocity) of a gas, and the start of fluidization is determined by the presence of an inflection point.

[0034] Such determination of the fluidized state of the solid reactant layer will be described in further detail in Examples.

[0035] When the solid reactant is brought into contact with the material gas containing HFC-134a, the solid reactant may be in a solid phase or may be dispersed in a medium in a liquid phase. As a solvent in which the solid reactant is dispersed, for example, water, an alcohol solvent such as methanol or ethanol, or a chlorinated solvent such as carbon tetrachloride may be mentioned. Since by contact in a state where the solid reactant is dispersed in a medium in a liquid phase, the pressure in the reaction system tends to be too high and high temperature reaction tends to be difficult, and accordingly it is preferred that the solid reactant is a solid phase and is brought into contact with the material gas in a gaseous phase.

[0036] The specific surface area of the solid reactant is preferably from 1 to 400 m^2/g, more preferably from 1 to 200 m^2/g. In this specification, the specific surface area is a value measured by a BET method (BET specific surface area). If the specific surface area of the solid reactant is less than 1 m^2/g, the reaction rate tends to be low, and the reaction efficiency tends to be low. Further, if the specific surface are exceeds 400 m^2/g, the density of the solid reactant particles tends to be too low, and thus the particles are likely to fly and the handling efficiency is thereby low.

[0037] The bulk density of the solid reactant is preferably from 0.2 to 3.0 g/cm^3, more preferably from 0.5 to 2.9 g/cm^3, particularly preferably from 0.7 to 2.5 g/cm^3. If the bulk density of the solid reactant is less than 0.2 g/cm^3, the volume at the same mass tends to be large, and not only a large-sized reactor is necessary, but also the particles of the solid reactant are likely to fly and the handling efficiency is thereby low, thus leading to a poor production efficiency. Further, if the bulk density of the solid reactant is higher than 3.0 g/cm^3, the rate of the material gas required to fluidize the particles of the solid reactant tends to be too high. Accordingly, in order to secure a sufficient contact time for the reaction with HFC-134a, a large-sized reactor will be necessary, and the production efficiency tends to be poor.

[0038] The solid reactant used in the present invention contains a compound which relates to the reaction mechanism represented by the reaction formula (1) or (2) as a representative example. The compound which may relate to the reaction mechanism represented by the reaction formula (1) or (2) as a representative example may, for example, be at least one compound selected from a metal oxide, a metal hydroxide, a metal carbonate, a metal sulfate and a metal halide. Preferred is a metal oxide or a metal carbonate, whereby HFC-134a will be efficiently converted to HFO-1123. The solid reactant may be used alone or in combination of two or more.

[0039] The metal species contained in the metal compound may be an alkali metal, an alkaline earth metal, a transition metal, a group 12 metal, a group 13 metal or a group 14 metal. Among them, preferred is an alkali metal, an alkaline earth metal, a group 13 metal or a group 14 metal, particularly preferred is sodium, potassium, calcium, magnesium, aluminum or silicon.

[0040] The metal oxide may be an oxide of one of the above metals or may be a composite oxide of two or more metals.

[0041] The metal hydroxide may be a hydroxide of one of the above metals or may be a composite hydroxide of two or more metals.

[0042] The metal carbonate may be a carbonate of one of the above metals or may be a composite carbonate of two or more metals.

[0043] The metal sulfate may be a sulfate of one of the above metals or may be a composite sulfate of two or more metals.

[0044] The metal halide may be a halide of one of the above metals or may be a composite halide of two or more metals.

[0045] Specifically, the solid reactant may, for example, be potassium carbonate, calcium hydroxide, calcium oxide, magnesium oxide, aluminum fluoride or aluminum oxide (alumina). In order that HFC-134a is converted to HFO-1123 efficiently, the solid reactant is particularly preferably potassium carbonate or calcium oxide.

[0046] The solid reactant in the present invention may be constituted solely by the above compound which may relate to the reaction mechanism represented by the reaction formula (1) or (2) as a representative example or may contain another component. Such another component which the solid reactant may contain may, for example, be a carrier to support the compound which may relate to the reaction mechanism represented by the reaction formula (1) or (2) as a representative example. The carrier may, for example, be an alumina carrier, a zirconia carrier, a silica carrier, a silicaalumina carrier, a carbon carrier represented by activated carbon, a barium sulfate carrier or a calcium carbonate carrier. Activated carbon may, for example, be activated carbon prepared from a material such as wood, charcoal, fruit shell, coconut shell, peat, lignite or coal.

(Reaction conditions)

[0047] The material gas containing HFC-134a may be introduced to a reactor (for example, a fluidized bed reactor) as it is at room temperature, but is preferably heated (preheated) before introduced to a reactor and then supplied, so as to increase the reactivity. In a case where it is preheated, the material gas is preferably heated to a temperature of from 80 to 450°C and then supplied to a reactor. Further, the respective components (HFC-134a and the diluent gas) in the material gas containing HFC-134a may be respectively preheated to the above temperature and then mixed, and the mixed material gas at the above temperature is supplied to a reactor, or the respective components may be mixed first, and then the material gas is heated to the above temperature and supplied to a reactor. Further, the respective components for the material gas may be respectively preheated to the above temperature and separately supplied to a reactor.

[0048] When the material gas containing HFC-134a is supplied, in order that the linear velocity of the material gas in the reactor is within a predetermined range, the flow rates per unit time (hereinafter referred to simply as flow rate) of HFC-134a and the diluent gas are preferably set. The linear velocity of the material gas is preferably from 1 cm/s to 1,000 cm/s, more preferably from 1 cm/s to 20 cm/s. Here, the linear velocity means a superficial velocity, and is calculated, assuming that the reactor through which the material gas flows is a void tower having no content in the interior thereof, by dividing the flow rate (volume flow rate) at the temperature under the pressure in the interior of the reactor by the cross section area of the reactor which is a void tower.

[0049] Linear velocity (superficial velocity) (cm/s) = flow rate (cm^3/s) / cross section area (cm^2)

[0050] In such a manner, the material gas containing HFC-134a introduced to the reactor is brought into contact with the solid reactor in a fluidized state forming the fluid bed (fluidized bed) in the reactor for a predetermined time. The temperature at the time of contact is preferably from 50 to 500°C, more preferably from 100 to 500°C, particularly preferably from 350 to 500°C as the temperature in the interior of the reactor, with a view to improving the reactivity. The pressure in the reactor is preferably from 0 to 5 MPa, more preferably from 0 to 1 MPa by the gauge pressure. The contact time of HFC-134a and the solid reactant in the reactor is preferably from 0.1 to 500 seconds, more preferably from 0.1 to 100 seconds, further preferably from 0.1 to 20 seconds.

(Reaction apparatus)

[0051] An example of a reaction apparatus used for production of HFO-1123 in the present invention is shown in Fig. 1. A fluidized bed reaction apparatus 1 shown in Fig. 1 comprises an electric furnace or an electric heater 2a and in its inside, a vertical fluidized bed reactor 2. A heating means such as an electric furnace or an electric heater 2a is not essential.

[0052] In the fluidized bed reactor 2, a solid reactant layer 3 of e.g. potassium carbonate is accommodated to form a vertical fluidized bed. Further, to the lower portion of the fluidized bed reactor 2, a preheating mixer 4 provided with a heating means such as an electric heater is connected via a material gas supply line 5. The material gas supply line 5 is preferably also provided with a heating means such as an electric heater. To the preheating mixer 4, a HFC-134a supply line 6 to supply HFC-134a which is gaseous at room temperature and a diluent gas supply line 7 which supplies a diluent gas are connected. HFC-134a and a diluent gas are supplied to the preheating mixer 4 respectively from the HFC-134a supply line 6 and the diluent gas supply line 7, mixed in the preheating mixer 4 and heated to a predetermined temperature, and the mixture is supplied to the fluidized bed reactor 2 through the material gas supply line 5.

[0053] Further, as shown in Fig. 1, the HFC-134a supply line 6 and the diluent gas supply line 7 may be combined before the preheating mixer 4, so that HFC-134a and the diluent gas are mixed and the mixture is supplied to the preheating mixer 4 via a gas mixture supply line (not shown), or the HFC-134a supply line 6 and the diluent gas supply

line 7 may be respectively connected to the preheating mixer 4, so that HFC-134a and the diluent gas are separately supplied to the preheating mixer 4. Further, at least one of the HFC-134a supply line 6 and the diluent gas supply line 7 may be provided with a preheater (not shown) provided with e.g. an electric heater, so that at least one of HFC-134a and the diluent gas supplied through the line is heated and then introduced to the preheating mixer 4.

[0054] To the outlet on the upper portion of the fluidized bed reactor 2, an outlet line 9 provided with a heating means 8 such as an electric heater is connected, and the outlet line 9 is provided with a hydrogen fluoride trapping tube 10. Hydrogen fluoride is removed from a gas discharged from the outlet of the fluidized bed reactor 2 (hereinafter referred to as an outlet gas) by the hydrogen fluoride trapping tube 10, and the outlet gas is collected into a sampling bag, and its components are analyzed by an analyzer such as a gas chromatograph (GC) and determined.

(Outlet gas component)

[0055] In the production method of the present invention, HFO-1123 can be obtained as a component in the outlet gas. Compounds other than HFO-1123 and an unreacted material component (HFC-134a) contained in the outlet gas may, for example, be hydrogen fluoride, E/Z-1,2-difluoroethylene (E/Z-HFO-1132), 1,1-difluoroethylene (VdF), 1,1,2-trifluoroethane (HFC-143), methane, ethane, ethylene, propane, propylene, n-butane, isobutane, 1-n-butene, 2-n-butene, isobutene, fluoroethylene (HFO-1141), 3,3-difluoropropene (HFO-1252zf), 3,3,3-trifluoropropene (HFO-1243zf), 2,3,3,3-tetrafluoropropene (HFO-1234yf), E/Z-1,3,3,3-tetrafluoropropene (E/Z-HFO-1234ze), hexafluoropropylene (HFP), HFC-125, HFC-134, 1,1,1-trifluoroethane (HFC-143a), 1,1,1,2,2,3,3-heptafluoropropane (HFC-227ca), 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea), 1,1,1,3,3,3-hexafluoropropane (HFC-236fa), 1,1,1,2,3,3-hexafluoropropane (HFC-236ea), HFC-32, trifluoromethane (HFC-23), fluoromethane (HFC-41), carbon monoxide, carbon dioxide and water. In the above description, E/Z means a mixture of E-form and Z-form.

[0056] The compound obtained as the outlet gas component may be used as it is for various applications, but is preferably used after purification to improve the purity of HFO-1123 as a desired component. The purification method may, for example, be distillation, adsorption or washing with an acidic aqueous solution, a basic aqueous solution or a neutral aqueous solution. The components other than HFO-1123 contained in the outlet gas may be separated and removed to a desired extent by the above means. Among the above purification methods, preferred is distillation under normal pressure, elevated pressure or reduced pressure, and by distillation under such a pressure, high purity HFO-1123 can be obtained. Further, HFC-134a separated from the outlet gas may be recycled as a part of the material gas.

EXAMPLES

[0057] Now, the present invention will be described in detail with reference to Examples. However, it should be understood that the present invention is by no means restricted to such specific Examples. In the following description, the preheat temperature of HFC-134a, and the temperature and the pressure in the reactor are set values. A. Synthesis reaction using potassium carbonate as solid reactant

(Analysis conditions)

[0058] To analyze the composition of the outlet gas, gas chromatography (GC) was employed. As a column, DB-1 (manufactured by Agilent Technologies, length: 60 m × inner diameter: 250 μm × thickness: 1 μm) was used.

(Reaction apparatus 1)

[0059] As a reaction apparatus 1, a fluidized bed reaction apparatus 11 shown in Fig. 2 was used. The fluidized bed reaction apparatus 11 shown in Fig. 2 comprises the fluidized bed reaction apparatus 1 shown in Fig. 1, provided with a differential pressure measuring device to measure a differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor 2.

[0060] In the fluidized bed reaction apparatus 11, as the fluidized bed reactor 2, a reactor for a vertical fluidized bed having an inner diameter of 21.4 mm and a height of 600 mm made of stainless steel (SUS316) was used, a SUS316 insertion tube having a diameter of 3.1 mm was introduced to the center of the reactor, a type K thermocouple was inserted to the insertion tube, and the temperature in the reactor was measured. Further, a grating and glass wool were disposed at a height of 100 mm from the lower portion of the fluidized bed reactor 2, and a solid reactant was packed thereon to form a solid reactant layer 3. The interior of the fluidized bed reactor 2 was heated by an electric furnace 2a.

[0061] A preheating mixer 4 was connected to the lower portion of the fluidized bed reactor 2 via a material gas supply line 5. The material gas supply line 5 and the preheating mixer 4 were respectively heated to 100°C by a ribbon heater. The apparatus was so constituted that HFC-134a and nitrogen as a diluent gas were mixed while their flow rates were adjusted respectively by mass flow controllers 6a and 7a provided to a HFC-134a supply line 6 and a diluent gas supply

line 7, and the gas mixture was supplied to the preheating mixer 4 through a gas mixture supply line 12. The outlet gas containing a reaction product was continuously withdrawn from the upper portion of the fluidized bed reactor 2, made to flow through a hydrogen fluoride trapping tube 10 packed with 28 g of 1/16 inch sodium fluoride pellets, collected in a sampling bag made of polyvinylidene fluoride (PVdF) (hereinafter referred to as PVdF bag), and subjected to composition analysis by means of gas chromatography (GC).

[0062] Further, the differential pressure measuring device was constituted as follows. That is, between an inlet side piping connected to the lower portion of the fluidized bed reactor 2 and an outlet side piping connected to the upper portion, a semitransparent PFA tube 13a having an inner diameter of 4.35 mm, processed into a U-shape having a height of 600 mm in a vertical direction was inserted, and a fluorine oil (density: 1.85 g/mL (25°C)) was introduced to the tube to a height of 300 mm, thereby to constitute a differential pressure gauge 13.

(Fluidization visualized test apparatus)

[0063] In the fluidized bed reaction apparatus 1 shown in Fig. 1, a visualized tester 14 having the same inner diameter and height (inner diameter: 21.4 mm × height: 600 mm) as the fluidized bed reactor 2, made of a transparent acrylic resin so that the flow state in the interior was visible, was disposed to constitute a fluidization visualized test apparatus 15. In the visualized tester 14, in the same manner as in the fluidized bed reactor 2 of the fluidized bed reaction apparatus 1, a grating and glass wool were disposed at a height of 100 mm from the lower portion, and a solid reactant was packed thereon to form a solid reactant layer 3. Further, to the lower portion of the visualized tester 14, a gas mixture supply line 12 to supply a gas mixture of HFC-134a and a diluent gas was connected. HFC-134a and nitrogen were mixed while their flow rates were adjusted by mass flow controllers 6a and 7a disposed to a HFC-134a supply line 6 and a diluent gas supply line 7, and the gas mixture is supplied to the visualized tester 14 by the mixed gas supply line 12.

[0064] Further, a differential pressure measuring device was provided so as to measure the differential pressure between on the inlet side on the outlet side of the visualized tester 14. That is, a differential pressure gauge 13 was provided in the same manner as the fluidized bed reaction apparatus 11 shown in Fig. 2, between an inlet side piping connected to the lower portion of the visualized tester 14 and an outlet side piping connected to the upper portion.

(Linear velocity)

[0065] The linear velocity of each of a nitrogen gas and a gas mixture of nitrogen and HFC-134a was obtained by dividing the flow rate (volume flow rate) per unit time of each gas at the reaction temperature under the reaction pressure by the cross section area of the fluidized bed reactor 2 or the visualized tester 14.

Reactant Packing Example 1

[0066] The visualized tester of the fluidization visualized test apparatus was packed with 55 g of particulate potassium carbonate (manufactured by Asahi Glass Company, Limited, tradename: potassium carbonate FG, average particle size: 300 μm, bulk density: 0.9 g/cm^3, specific surface area: 1.2 m^2/g (hereinafter referred to as potassium carbonate FG)) as a solid reactant to a height of 150 mm.

Reactant Packing Example 2

[0067] The fluidized bed reactor of the fluidized bed reaction apparatus 11 was packed with 55 g of particulate potassium carbonate FG to a height of 150 mm.

Reactant Packing Example 3

[0068] The visualized tester of the fluidization visualized test apparatus was packed with 24 g of particulate potassium carbonate (manufactured by Asahi Glass Company, Limited, tradename: potassium carbonate FG R-10, average particle size: 10 μm, bulk density: 0.3 g/cm^3, specific surface area: 1.4 m^2/g (hereinafter referred to as potassium carbonate FG R-10)) to a height of 150 mm.

Reactant Packing Example 4

[0069] The fluidized bed reactor of the fluidized bed reaction apparatus 11 was packed with 24 g of particulate potassium carbonate FG R-10 to a height of 150 mm.

Fluidization Example 1

[0070] Through the fluidization visualized test apparatus packed with the solid reactant (potassium carbonate FG having an average particle size of 300 μm) shown in Reactant Packing Example 1, a nitrogen gas was made to flow at a flow rate of 151 mmol/min (linear velocity of 17 cm/s) at room temperature (25°C) under normal pressure. On that occasion, the differential pressure between on the inlet side and on the outlet side of the visualized tester measured by the differential pressure gauge was 1,960 Pa Further, in the visualized tester, mixing of an upper portion and a lower portion was observed in the entire layer of the solid reactant. That is, a completely fluidized state was visually confirmed.

[0071] Here, the fluidized state by visual observation of the solid reactant layer in the visualized tester was evaluated under the following standards.

○: The upper portion and the lower portion are mixed in the entire layer of the solid reactant packed (completely fluidized state).

Δ: The upper portion and the lower portion are mixed only in a part of the layer of the solid reactant packed (partially fluidized state).

×: The upper portion and the lower portion of the layer of the solid reactant packed are not mixed (non-fluidized state).

[0072] Then, the flow rate of the nitrogen gas was gradually decreased, and the differential pressure between on the inlet side and on the outlet side of the visualized tester was measured by the differential pressure gauge at each flow rate, and the fluidized state of the solid reactant in the visualized tester was visually examined. The flow rate of the nitrogen gas, the linear velocity, the differential pressure and the fluidized state of the solid reactant visually observed are shown in Table 1. Further, a graph obtained by plotting the differential pressure relative to the linear velocity of the nitrogen gas is shown in Fig. 4.

[0073] In the graph obtained by plotting the differential pressure relative to the linear velocity of the gas, the inflection point at which the gradient of the graph changes is taken as the starting point of fluidization of the solid reactant layer, and the linear velocity at the inflection point may be taken as the fluidization starting velocity. Further, in a graph having two inflection points in the differential pressure, the linear velocity at an inflection point on the lower linear velocity side is taken as the partial fluidization starting velocity, and the linear velocity at an inflection point on the higher linear velocity side is taken as the complete fluidization starting velocity. It can be judged from Table 1 and Fig. 4 that in Fluidization Example 1, the partial fluidization starting velocity of the solid reactant layer is from 3 to 6 cm/s, and the complete fluidization starting velocity is 13 cm/s.

[Table 1]

Fluidization Example 1																	
Temp. °C		25															
Gas composition ratio	HFC-134a mol%	0															
	Nitrogen mol%	100															
Flow rate	HFC-134a mmol/min	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Nitrogen mmol/min	151	142	134	125	116	107	98	89	80	71	62	53	44	35	27	18
Linear velocity cm/s		17	16	15	14	13	12	11	10	9	8	7	6	5	4	3	2
Differential pressure Pa		1960	1942	1905	1887	1869	1833	1760	1706	1669	1615	1542	1397	1252	1071	853	617
Fluidized state by visual observation		○	○	○	○	○	Δ	Δ	Δ	Δ	Δ	Δ	Δ	Δ	Δ	Δ	×

Fluidization Example 2

[0074] Through the fluidization visualized test apparatus packed with the solid reactant (potassium carbonate FG) shown in Reactant Packing Example 1, a nitrogen gas at a flow rate of 121 mmol/min and HFC-134a at a flow rate of 30 mmol/min were mixed at room temperature (25°C) under normal pressure and made to flow. That is, 80 mol% of a nitrogen gas and 20 mol% of HFC-134a were mixed and made to flow (linear velocity of gas mixture of 17 cm/s). On that occasion, the differential pressure between on the inlet side and on the outlet side of the visualized tester measured by the differential pressure gauge was 2,395 Pa. Further, in the visualized tester, mixing of an upper portion and a lower portion was observed in the entire layer of the solid reactant, and a completely fluidized state was visually confirmed.

[0075] Then, while the composition of HFC-134a and nitrogen (HFC-134a: N_2=20:80 (by mol%)) was kept, the nitrogen gas flow rate and the HFC-134a flow rate were gradually decreased, and at each flow rate, the differential pressure between on the inlet side and on the outlet side of the visualized tester was measured by the differential pressure gauge, and the fluidized state of the solid reactant in the visualized tester was visually examined. The flow rate of the nitrogen gas, the flow rate of HFC-134a, the linear velocity of the gas mixture, the differential pressure, and the fluidized state of the solid reactant visually observed are shown in Table 2. Further, a graph obtained by plotting the differential pressure relative to the linear velocity of the gas mixture is shown in Fig. 5. It can be judged from Table 2 and Fig. 5 that in Fluidization Example 2, the partial fluidization starting velocity of the solid reactant layer is from 4 to 8 cm/s, and the complete fluidization starting velocity is 15 cm/s.

[Table 2]

Fluidization Example 2																		
Temp. °C			25															
Gas composition ratio	HFC-134a mol%		20															
	Nitrogen mol%		80															
Flow rate	HFC-134a mmol/min		30	29	27	25	23	21	20	18	16	14	12	11	9	7	5	4
	Nitrogen mmol/min		121	114	107	100	93	86	78	71	64	57	50	43	36	28	21	14
Linear velocity cm/s			17	16	15	14	13	12	11	10	9	8	7	6	5	4	3	2
Differential pressure Pa			2395	2341	2286	2177	2105	2032	1960	1887	1815	1724	1597	1433	1252	1034	835	581
Fluidized state by visual observation			○	○	○	Δ	Δ	Δ	Δ	Δ	Δ	Δ	Δ	Δ	Δ	Δ	×	×

Fluidization Example 3

[0076] Through the fluidized bed reaction apparatus packed with the solid reactant (potassium carbonate FG) shown in Reactant Packing Example 2, a nitrogen gas was made to flow at a flow rate of 152 mmol/min (linear velocity of 17 cm/s) at room temperature (25°C) under normal pressure. On that occasion, the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor measured by the differential pressure gauge was 2,631 Pa.

[0077] Then, the nitrogen gas flow rate was gradually decreased, and at each flow rate, the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor was measured by the differential pressure gauge. The flow rate of the nitrogen gas, the linear velocity and the differential pressure are shown in Table 3. Further, a graph obtained by plotting the differential pressure relative to the linear velocity of the nitrogen gas is shown in Fig. 6. It can be judged from Table 3 and Fig. 6 that in Fluidization Example 3, the partial fluidization starting velocity of the solid reactant layer is 6 cm/s, and the complete fluidization starting velocity is 15 cm/s.

[Table 3]

Fluidization Example 3																	
Temp. °C		25															
Gas composition ratio	HFC-134a mol%	0															
	Nitrogen mol%	100															
Flow rate	HFC-134a mmol/min	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Nitrogen mmol/min	152	143	134	125	116	107	98	89	80	71	62	53	44	35	27	18
Linear velocity cm/s		17	16	15	14	13	12	11	10	9	8	7	6	5	4	3	2
Differential pressure Pa		2631	2595	2522	2359	2268	2159	2087	1960	1869	1760	1669	1579	1361	1107	853	599
Fluidized state by visual observation		-	-	-	-	-	-	-	-	-	-	-		-	-	-	-

Fluidization Example 4

[0078] Through the fluidized bed reaction apparatus packed with the solid reactant shown in Reactant Packing Example 2, a nitrogen gas at a flow rate of 143 mmol/min and

[0079] HFC-134a at a flow rate of 36 mmol/min were mixed at room temperature (25°C) under normal pressure and made to flow. That is, 80 mol% of a nitrogen gas and 20 mol% of HFC-134a were mixed and made to flow (linear velocity of gas mixture of 20 cm/s). On that occasion, the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor measured by the differential pressure gauge was 3,248 Pa.

[0080] Then, while the composition of HFC-134a and nitrogen (HFC-134a:N_2 = 20:80 (by mol%)) was kept, the nitrogen gas flow rate and the HFC-134a flow rate were gradually decreased, and at each flow rate, the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor was measured by the differential pressure gauge. The flow rate of the nitrogen gas, the flow rate of HFC-134a, the linear velocity of the gas mixture and the differential pressure are shown in Table 4. Further, a graph obtained by plotting the differential pressure relative to the linear velocity of the gas mixture is shown in Fig. 7. It can be judged from Table 4 and Fig. 7 that in Fluidization Example 4, the partial fluidization starting velocity of the solid reactant layer is 7 cm/s, and the complete fluidization starting velocity is 18 cm/s.

[Table 4]

		Fluidization Example 4									
Temp. °C		25									
Gas composition ratio	HFC-134a mol%	0									
	Nitrogen mol%	100									
Flow rate	HFC-134a mmol/min	36	34	32	30	29	27	25	23	21	20
	Nitrogen mmol/min	143	136	129	122	114	107	100	93	86	78
Linear velocity cm/s		20	19	18	17	16	15	14	13	12	11
Differential pressure Pa		3248	3175	3048	2958	2831	2722	2613	2468	2341	2214
Fluidized state by visual observation		-	-	-	-	-	-	-	-	-	-

[Table 4] (continued)

		Fluidization Example 4								
Temp. °C		25								
Gas composition ratio	HFC-134a mol%	0								
	Nitrogen mol%	100								
Flow rate	HFC-134a mmol/min	18	16	14	12	11	9	7	5	4
	Nitrogen mmol/min	71	64	57	50	43	36	28	21	14
Linear velocity cm/s		10	9	8	7	6	5	4	3	2
Differential pressure Pa		2087	1978	1869	1742	1542	1288	1052	817	563
Fluidized state by visual observation		-	-	-	-	-	-	-	-	-

Fluidization Example 5

[0081] The interior of the fluidized bed reactor of the fluidized bed reaction apparatus packed with the solid reactant shown in Reactant Packing Example 2 was heated to 310°C by an electric furnace. A nitrogen gas was made to flow through the apparatus at a flow rate of 91 mmol/min (linear velocity of 20 cm/s) under normal pressure. On that occasion, the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor measured by the differential pressure gauge was 2,558 Pa.

[0082] Then, the nitrogen gas flow rate was gradually decreased, and at each flow rate, the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor was measured by the differential pressure gauge. The flow rate of the nitrogen gas, the linear velocity and the differential pressure are shown in Table 5. Further, a graph obtained by plotting the differential pressure relative to the linear velocity of the nitrogen gas is shown in Fig. 8.

It can be judged from Table 5 and Fig. 8 that in Fluidization Example 5, the partial fluidization starting velocity of the solid reactant layer is 6 cm/s, and the complete fluidization starting velocity is 10 cm/s.

[Table 5]

		Fluidization Example 5									
Temp. °C		310									
Gas composition ratio	HFC-134a mol%	0									
	Nitrogen mol%	100									
Flow rate	HFC-134a mmol/min	0	0	0	0	0	0	0	0	0	0
	Nitrogen mmol/min	91	87	82	78	73	68	64	59	55	50
Linear velocity cm/s		20	19	18	17	16	15	14	13	12	11
Differential pressure Pa		2558	2504	2395	2341	2250	2177	2087	1996	1905	1815
Fluidized state by visual observation		-	-	-	-	-	-	-	-	-	-

[Table 5] (continued)

		Fluidization Example 5								
Temp. °C		310								
Gas composition ratio	HFC-134a mol%	0								
	Nitrogen mol%	100								
Flow rate	HFC-134a mmol/min	0	0	0	0	0	0	0	0	0
	Nitrogen mmol/min	45	41	36	32	27	23	18	14	9
Linear velocity cm/s		10	9	8	7	6	5	4	3	2
Differential pressure Pa		1742	1633	1452	1361	1234	1071	780	726	490
Fluidized state by visual observation		-	-	-	-	-	-	-	-	-

Fluidization Example 6

[0083] The interior of the fluidized bed reactor of the fluidized bed reaction apparatus packed with the solid reactant shown in Reactant Packing Example 2 was heated to 360°C by an electric furnace. A nitrogen gas was made to flow through the apparatus at a flow rate of 84 mmol/min (linear velocity of 20 cm/s) under normal pressure. On that occasion, the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor measured by the differential pressure gauge was 2,431 Pa.

[0084] Then, the nitrogen gas flow rate was gradually decreased, and at each flow rate, the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor was measured by the differential pressure gauge. The flow rate of the nitrogen gas, the linear velocity and the differential pressure are shown in Table 6. Further, a graph obtained by plotting the differential pressure relative to the linear velocity of the nitrogen gas is shown in Fig. 9. It can be judged from Table 6 and Fig. 9 that in Fluidization Example 6, the partial fluidization starting velocity of the solid reactant layer is 7 cm/s, and the complete fluidization starting velocity is 10 cm/s.

[Table 6]

		Fluidization Example 6									
Temp. °C		360									
Gas composition ratio	HFC-134a mol%	0									
	Nitrogen mol%	100									
Flow rate	HFC-134a mmol/min	0	0	0	0	0	0	0	0	0	0
	Nitrogen mmol/min	84	80	76	71	67	63	59	55	50	46
Linear velocity cm/s		20	19	18	17	16	15	14	13	12	11
Differential pressure Pa		2431	2359	2304	2232	2159	2087	1996	1942	1851	1778
Fluidized state by visual observation		-	-	-	-	-	-	-	-	-	-

[Table 6] (continued)

		Fluidization Example 6								
Temp. °C		360								
Gas composition ratio	HFC-134a mol%	0								
	Nitrogen mol%	100								
Flow rate	HFC-134a mmol/min	0	0	0	0	0	0	0	0	0
	Nitrogen mmol/min	42	38	33	29	25	21	17	12	8
Linear velocity cm/s		10	9	8	7	6	5	4	3	2
Differential pressure Pa		1706	1560	1361	1179	1234	1016	798	599	508
Fluidized state by visual observation		-	-	-	-	-	-	-	-	-

Fluidization Example 7

[0085] The interior of the fluidized bed reactor of the fluidized bed reaction apparatus packed with the solid reactant shown in Reactant Packing Example 2 was heated to 410°C by an electric furnace. A nitrogen gas was made to flow through the apparatus at a flow rate of 78 mmol/min (linear velocity of 20 cm/s) under normal pressure. On that occasion, the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor measured by the differential pressure gauge was 2,431 Pa.

[0086] Then, the nitrogen gas flow rate was gradually decreased, and at each flow rate, the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor was measured by the differential pressure gauge. The flow rate of the nitrogen gas, the linear velocity and the differential pressure are shown in Table 7. Further, a graph obtained by plotting the differential pressure relative to the linear velocity of the nitrogen gas is shown in Fig. 10. It can be judged from Table 7 and Fig. 10 that in Fluidization Example 7, the partial fluidization starting velocity of the solid reactant layer is 8 cm/s, and the complete fluidization starting velocity is 10 cm/s.

[Table 7]

		Fluidization Example 7								
Temp. °C		410								
Gas composition ratio	HFC-134a mol%	0								
	Nitrogen mol%	100								
Flow rate	HFC-134a mmol/min	0	0	0	0	0	0	0	0	0
	Nitrogen mmol/min	78	74	70	66	62	58	54	51	47
Linear velocity cm/s		20	19	18	17	16	15	14	13	12
Differential pressure Pa		2431	2341	2268	2196	2123	2069	1996	1923	1851
Fluidized state by visual observation		-	-	-	-	-	-	-	-	-

[Table 7] (continued)

		Fluidization Example 7								
Temp. °C		410								
Gas composition ratio	HFC-134a mol%	0								
	Nitrogen mol%	100								
Flow rate	HFC-134a mmol/min	0	0	0	0	0	0	0	0	0
	Nitrogen mmol/min	43	39	35	31	27	23	19	15	12
Linear velocity cm/s		11	10	9	8	7	6	5	4	3
Differential pressure Pa		1778	1706	1633	1524	1107	962	798	653	490
Fluidized state by visual observation		-	-	-	-	-	-	-	-	-

Comparative Fluidization Example 1

[0087] Through the fluidization visualized test apparatus packed with the solid reactant (potassium carbonate FG R-10 having an average particle size of 10 μm) shown in Reactant Packing Example 3, a nitrogen gas was made to flow at a flow rate of 90 mmol/min (linear velocity of 10 cm/s) at room temperature (25°C) under normal pressure. On that occasion, the differential pressure between on the inlet side and on the outlet side of the visualized tester measured by the differential pressure gauge was 4,990 Pa. Further, in the fluidized tester, mixing of an upper portion and a lower portion of the layer of the solid reactant was not confirmed, and the solid reactant layer formed a flow path and was in a single flow state. That is, the solid reactant layer was not fluidized.

[0088] Then, the nitrogen gas flow rate was gradually decreased, and at each flow rate, the differential pressure between on the inlet side and on the outlet side of the visualized tester was measured by the differential pressure gauge, and the fluidized state of the solid reactant in the visualized tester was visually examined. The flow rate of the nitrogen gas, the linear velocity, the differential pressure and the fluidized state of the solid reactant by visual observation are shown in Table 8. Further, a graph obtained by plotting the differential pressure relative to the linear velocity of the nitrogen gas is shown in Fig. 11. In the graph shown in Fig. 11, no inflection point of the differential pressure indicating the start of fluidization of the solid reactant layer was observed. It can be judged from Table 8 and Fig. 11 that in Comparative Fluidization Example 1, within a range of the linear velocity of at most 10 cm/s, no fluidization including partial fluidization occurred.

[Table 8]

		Comparative Fluidization Example 1								
Temp. °C		25								
Gas composition ratio	HFC-134a mol%	0								
	Nitrogen mol%	100								
Flow rate	HFC-134a mmol/min	0	0	0	0	0	0	0	0	0
	Nitrogen mmol/min	90	86	81	77	72	67	63	58	54
Linear velocity cm/s		10.0	9.5	9.0	8.5	8.0	7.5	7.0	6.5	6.0
Differential pressure Pa		4990	4754	4500	4264	4028	3774	3502	3302	3048
Fluidized state by visual observation		×	×	×	×	×	×	×	×	×

[Table 8] (continued)

		Comparative Fluidization Example 1								
Temp. °C		25								
Gas composition ratio	HFC-134a mol%	0								
	Nitrogen mol%	100								
Flow rate	HFC-134a mmol/min	0	0	0	0	0	0	0	0	0
	Nitrogen mmol/min	49	45	40	36	31	27	22	18	13
Linear velocity cm/s		5.5	5.0	4.5	4.0	3.5	3.0	2.5	2.0	1.5
Differential pressure Pa		2831	2558	2323	2105	1869	1651	1415	1143	944
Fluidized state by visual observation		×	×	×	×	×	×	×	×	×

Comparative Fluidization Example 2

[0089] Through the fluidized bed reaction apparatus packed with the solid reactant (potassium carbonate FG R-10) shown in Reactant Packing Example 4, a nitrogen gas was made to flow at a flow rate of 89 mmol/min (linear velocity of 10 cm/s) at room temperature (25°C) under normal pressure. On that occasion, the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor measured by the differential pressure gauge was 1,942 Pa.

[0090] Then, the nitrogen gas flow rate was gradually decreased, and at each flow rate, the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor was measured by the differential pressure gauge. The flow rate of the nitrogen gas, the linear velocity and the differential pressure are shown in Table 9. Further, a graph obtained by plotting the differential pressure relative to the linear velocity of the nitrogen gas is shown in Fig. 12. In the graph shown in Fig. 12, no inflection point of the differential pressure indicating the start of fluidization of the solid reactant layer was observed. It can be judged from Table 9 and Fig. 12 that in Comparative Fluidization Example 2, within a range of the linear velocity of at most 10 cm/s, no fluidization including partial fluidization occurred.

[Table 9]

		Comparative Fluidization Example 2								
Temp. °C		25								
Gas composition ratio	HFC-134a mol%	0								
	Nitrogen mol%	100								
Flow rate	HFC-134a mmol/min	0	0	0	0	0	0	0	0	0
	Nitrogen mmol/min	89	85	80	76	71	67	62	58	53
Linear velocity cm/s		10.0	9.5	9.0	8.5	8.0	7.5	7.0	6.5	6.0
Differential pressure Pa		1942	1833	1742	1597	1488	1379	1270	1161	1052
Fluidized state by visual observation		-	-	-	-	-	-	-	-	-

[Table 9] (continued)

		Comparative Fluidization Example 2								
Temp. °C		25								
Gas composition ratio	HFC-134a mol%	0								
	Nitrogen mol%	100								
Flow rate	HFC-134a mmol/min	0	0	0	0	0	0	0	0	0
	Nitrogen mmol/min	49	44	40	35	31	27	22	18	13
Linear velocity cm/s		5.5	5.0	4.5	4.0	3.5	3.0	2.5	2.0	1.5
Differential pressure Pa		944	853	762	671	581	490	399	327	200
Fluidized state by visual observation		-	-	-	-	-	-	-	-	-

Comparative Fluidization Example 3

[0091] The interior of the fluidized bed reactor of the fluidized bed reaction apparatus packed with the solid reactant shown in Reactant Packing Example 4 was heated to 310°C by an electric furnace. A nitrogen gas was made to flow through the apparatus at a flow rate of 89 mmol/min (linear velocity of 8.5 cm/s) under normal pressure. On that occasion, the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor measured by the differential pressure gauge was 1,688 Pa.

[0092] Then, the nitrogen gas flow rate was gradually decreased, and at each flow rate, the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor was measured by the differential pressure gauge. The flow rate of the nitrogen gas, the linear velocity and the differential pressure are shown in Table 10. Further, a graph obtained by plotting the differential pressure relative to the linear velocity of the nitrogen gas is shown in Fig. 13. In the graph shown in Fig. 13, no inflection point in the differential pressure indicating the start of fluidization of the solid reactant layer was observed. It can be judged from Table 10 and Fig. 13 that in Comparative Fluidization Example 3, within a range of the linear velocity of at most 8.5 cm/s, no fluidization including partial fluidization occurred.

[Table 10]

		Comparative Fluidization Example 3									
Temp. °C		310									
Gas composition ratio	HFC-134a mol%	0									
	Nitrogen mol%	100									
Flow rate	HFC-134a mmol/min	0	0	0	0	0	0	0	0	0	0
	Nitrogen mmol/min	39	37	35	33	31	29	27	25	23	21
Linear velocity cm/s		8.5	8.1	7.7	7.3	6.8	6.4	6.0	5.5	5.1	4.7
Differential pressure Pa		1688	1542	1470	1379	1288	1216	1125	1034	962	871
Fluidized state by visual observation		-	-	-	-	-	-	-	-	-	-

[Table 10] (continued)

		Comparative Fluidization Example 3									
Temp. °C		310									
Gas composition ratio	HFC-134a mol%	0									
	Nitrogen mol%	100									
Flow rate	HFC-134a mmol/min	0	0	0	0	0	0	0	0	0	0
	Nitrogen mmol/min	19	17	15	14	12	10	8	6	4	2
Linear velocity cm/s		4.3	3.8	3.4	3.0	2.6	2.1	1.7	1.3	0.9	0.4
Differential pressure Pa		798	708	635	563	454	381	290	200	127	73
Fluidized state by visual observation		-	-	-	-	-	-	-	-	-	-

Comparative Fluidization Example 4

[0093] The interior of the fluidized bed reactor of the fluidized bed reaction apparatus packed with the solid reactant shown in Reactant Packing Example 4 was heated to 360°C by an electric furnace. A nitrogen gas was made to flow through the apparatus at a flow rate of 36 mmol/min (linear velocity of 8.5 cm/s) under normal pressure. On that occasion, the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor measured by the differential pressure gauge was 2,087 Pa.

[0094] Then, the nitrogen gas flow rate was gradually decreased, and at each flow rate, the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor was measured by the differential pressure gauge. The flow rate of the nitrogen gas, the linear velocity and the differential pressure are shown in Table 11. Further, a graph obtained by plotting the differential pressure relative to the linear velocity of the nitrogen gas is shown in Fig. 14. In the graph shown in Fig. 14, no inflection point in the differential pressure indicating the start of fluidization of the solid reactant layer was observed. It can be judged from Table 11 and Fig. 14 that in Comparative Fluidization Example 4, within a range of the linear velocity of at most 8.5 cm/s, no fluidization including partial fluidization occurred.

[Table 11]

			Comparative Fluidization Example 4									
Temp.		°C	360									
Gas composition ratio	HFC-134a	mol%	0									
	Nitrogen	mol%	100									
Flow rate	HFC-134a	mmol/min	0	0	0	0	0	0	0	0	0	0
	Nitrogen	mmol/min	36	34	32	30	29	27	25	23	21	20
Linear velocity		cm/s	8.5	8.1	7.7	7.3	6.8	6.4	6.0	5.5	5.1	4.7
Differential pressure		Pa	2087	2050	1960	1851	2087	1887	1742	1597	1325	1179
Fluidized state by visual observation			-	-	-	-	-	-	-	-	-	-

[Table 11] (continued)

			Comparative Fluidization Example 4									
Temp.		°C	360									
Gas composition ratio	HFC-134a	mol%	0									
	Nitrogen	mol%	100									
Flow rate	HFC-134a	mmol/min	0	0	0	0	0	0	0	0	0	0
	Nitrogen	mmol/min	18	16	14	12	11	9	7	5	4	2
Linear velocity		cm/s	4.3	3.8	3.4	3.0	2.6	2.1	1.7	1.3	0.9	0.4
Differential pressure		Pa	1052	944	835	726	563	454	345	254	145.2	73
Fluidized state by visual observation			-	-	-	-	-	-	-	-	-	-

Comparative Fluidization Example 5

[0095] The interior of the fluidized bed reactor of the fluidized bed reaction apparatus packed with the solid reactant shown in Reactant Packing Example 4 was heated to 410°C by an electric furnace. A nitrogen gas was made to flow through the apparatus at a flow rate of 39 mmol/min (linear velocity of 10 cm/s) under normal pressure. On that occasion, the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor measured by the differential pressure gauge was 1,579 Pa.

[0096] Then, the nitrogen gas flow rate was gradually decreased, and at each flow rate, the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor was measured by the differential pressure gauge. The flow rate of the nitrogen gas, the linear velocity and the differential pressure are shown in Table 12. Further, a graph obtained by plotting the differential pressure relative to the linear velocity of the nitrogen gas is shown in Fig. 15. In the graph shown in Fig. 15, no inflection point in the differential pressure indicating the start of fluidization of the solid reactant layer was observed. It can be judged from Table 12 and Fig. 15 that in Comparative Fluidization Example 5, within a range of the linear velocity of at most 10 cm/s, no fluidization including partial fluidization occurred.

[Table 12]

		Comparative Fluidization Example 5									
Temp. °C		410									
Gas composition ratio	HFC-134a mol%	0									
	Nitrogen mol%	100									
Flow rate	HFC-134a mmol/min	0	0	0	0	0	0	0	0	0	0
	Nitrogen mmol/min	39	37	35	33	31	29	27	25	23	21
Linear velocity cm/s		10.0	9.5	9.0	8.5	8.0	7.5	7.0	6.5	6.0	5.5
Differential pressure Pa		1579	1488	1397	1288	1198	1107	1016	925	835	780
Fluidized state by visual observation		-	-	-	-	-	-	-	-	-	-

[Table 12] (continued)

		Comparative Fluidization Example 5									
Temp. °C		410									
Gas composition ratio	HFC-134a mol%	0									
	Nitrogen mol%	100									
Flow rate	HFC-134a mmol/min	0	0	0	0	0	0	0	0	0	0
	Nitrogen mmol/min	19	17	15	14	12	10	8	6	4	2
Linear velocity cm/s		5.0	4.5	4.0	3.5	3.0	2.5	2.0	1.5	1.0	0.5
Differential pressure Pa		708	635	581	526	544	454	363	272	145.2	54
Fluidized state by visual observation		-	-	-	-	-	-	-	-	-	-

[0097] The results of the fluidization tests in the above Fluidization Examples 1 to 7 and Comparative Fluidization Examples 1 to 5 are shown in Table 13. It is found from Table 13 that potassium carbonate having an average particle size of 300 μm has favorable flowability, and it can be in a fluidized state by making a gas to flow therethrough at a predetermined linear velocity, however, potassium carbonate having an average particle size of 10 μm is poor in the flowability, and it is not fluidized at a linear velocity of from several cm/s to a dozen cm/s.

[Table 13]

		Fluidization Example 1	Fluidization Example 2	Fluidization Example 3	Fluidization Example 4	Fluidization Example 5	Fluidization Example 6	Fluidization Example 7
Reactant Packing Example		Packing Example 1	Packing Example 1	Packing Example 2	Packing Example 2	Packing Example 2	Packing Example 2	Packing Example 2
Average particle size of potassium carbonate μm		300	300	300	300	300	300	300
Fluidization visualized test apparatus or fluidized bed reaction apparatus		Fluidization visualized test apparatus	Fluidization visualized test apparatus	Fluidized bed reaction apparatus	Fluidized bed reaction apparatus	Fluidized bed reaction apparatus	Fluidized bed reaction apparatus	Fluidized bed reaction apparatus
Temperature °C		25	25	25	25	310	360	410
Gas composition ratio	HFC-134a mol%	0	20	0	20	0	0	0
	Nitrogen mol%	100	80	100	80	100	100	100
Linear velocity/ differential pressure plot analysis	Partial fluidization starting velocity	6 cm/s	8 cm/s	6 cm/s	7 cm/s	6 cm/s	7 cm/s	8 cm/s
	Complete fluidization starting velocity	13 cm/s	15 cm/s	15 cm/s	18 cm/s	10 cm/s	10 cm/s	10 cm/s
Visual observation	Partial fluidization starting velocity	3 cm/s	4 cm/s	-	-	-	-	-
	Complete fluidization starting velocity	13 cm/s	15 cm/s	-	-	-	-	-

[Table 13] (continued)

		Comparative Fluidization Example 1	Comparative Fluidization Example 2	Comparative Fluidization Example 3	Comparative Fluidization Example 4	Comparative Fluidization Example 1
Reactant Packing Example		Packing Example 3	Packing Example 4	Packing Example 4	Packing Example 4	Packing Example 4
Average particle size of potassium carbonate μm		10	10	10	10	10
Fluidization visualized test apparatus or fluidized bed reaction apparatus		Fluidization visualized test apparatus	Fluidized bed reaction apparatus	Fluidized bed reaction apparatus	Fluidized bed reaction apparatus	Fluidized bed reaction apparatus
Temperature °C		25	25	310	360	410
Gas composition ratio	HFC-134a mol%	0	0	0	0	0
	Nitrogen mol%	100	100	100	100	100
Linear velocity/ differential pressure plot analysis	Partial fluidization starting velocity	No fluidization at less than 10 cm/s	No fluidization at less than 10 cm/s	No fluidization at less than 8.5 cm/s	No fluidization at less than 8.5 cm/s	No fluidization at less than 10 cm/s
	Complete fluidization starting velocity					
Visual observation	Partial fluidization starting velocity	No fluidization at less than 10 cm/s (single flow)	-	-	-	-
	Complete fluidization starting velocity		-	-	-	-

Examples 1 and 2

[0098] First, in Example 1, the interior of the fluidized bed reactor of the fluidized bed reaction apparatus packed with the solid reactant (potassium carbonate FG) shown in Reactant Packing Example 2 was heated by an electric furnace at 360°C. Then, a nitrogen gas was made to flow through the fluidized bed reaction apparatus at a flow rate of 50.3 mmol/min (linear velocity of 12 cm/s) under normal pressure. From the results of the fluidization test (Fluidization Example 6), it is considered that the layer of potassium carbonate FG was in a completely fluidized state at this linear velocity.

[0099] Then, while the flow rate of the nitrogen gas was kept, HFC-134a was started to be made to flow at a flow rate of 2.5 mmol/min. HFC-134a was made to flow and reacted for 10 minutes from the start of the flow of HFC-134a, and then only the supply of HFC-134a was terminated while the flow rate of the nitrogen gas was unchanged, to complete the reaction in Example 1. The outlet gas from 5 minutes after the start of the flow of HFC-134a to the completion of the reaction was continuously collected in a PVdF bag.

[0100] Then, after completion of the reaction in Example 1, without exchanging potassium carbonate in the fluidized bed reactor, Example 2 was carried out as it was. In Example 2, HFC-134a was brought into contact with and reacted with the solid reactant in the same manner as in Example 1 except that the reaction conditions were as identified in Table 14. Further, the composition of the outlet gas collected in the PVdF bag was analyzed by gas chromatography (GC). The analysis results are shown in Table 14 together with the reaction conditions (the nitrogen flow rate before the reaction, the reaction temperature, the HFC-134a flow rate at the time of the reaction, the nitrogen flow rate at the time of the reaction, the composition at the time of the reaction (HFC-134a: nitrogen (molar ratio)), the linear velocity at the time of the reaction, the contact time at the time of the reaction, presence or absence of the fluidized state at the time of the reaction, and the time over which HFC-134a was made to flow (hereinafter referred to as the reaction time)).

Comparative Examples 1 and 2

[0101] First, in Comparative Example 1, while the interior of the fluidized bed reactor of the fluidized bed reaction apparatus packed with the solid reactant (potassium carbonate FG R-10) shown in Reactant Packing Example 4 was heated to 360°C by an electric furnace, a nitrogen gas was made to flow through the fluidized bed reaction apparatus at a flow rate of 6.24 mmol/min (linear velocity of 1.5 cm/s) under normal pressure. From the results of the above fluidization test (Comparative Fluidization Example 4), it is considered that potassium carbonate FG R-10 was not fluidized at this linear velocity.

[0102] Then, while the flow rate of the nitrogen gas was kept, HFC-134a was started to be made to flow at a flow rate of 0.31 mmol/min. HFC-134a was made to flow and reacted for 15 minutes from the start of the flow of HFC-134a, and then only the supply of HFC-134a was terminated while the flow rate of the nitrogen gas was unchanged, to complete the reaction in Comparative Example 1. The outlet gas from 5 minutes after the start of the flow of HFC-134a to the completion of the reaction was continuously collected in a PVdF bag.

[0103] Then, after completion of the reaction in Comparative Example 1, without exchanging potassium carbonate in the fluidized bed reactor, Comparative Example 2 was conducted as it was. In Comparative Example 2, HFC-134a was brought into contact with and reacted with the solid reactant in the same manner as in Comparative Example 1 except that the reaction conditions were as identified in Table 15. And, the composition of the outlet gas collected in the PVdF bag was analyzed by gas chromatography (GC). The analysis results are shown in Table 15 together with the reaction conditions (the nitrogen flow rate before the reaction, the reaction temperature, the HFC-134a flow rate at the time of the reaction, the nitrogen flow rate at the time of the reaction, the composition at the time of the reaction (HFC-134a: nitrogen (molar ratio)), the linear velocity at the time of the reaction, the contact time at the time of the reaction, presence or absence of the fluidized state at the time of the reaction, and the reaction time).

[0104] Then, in Examples 1 and 2 and Comparative Examples 1 and 2, based on the area ratio (GC Area%) of the outlet gas obtained by gas chromatography analysis, the degree of conversion (reactivity) of HFC-134a, the selectivity for HFO-1123 and the selectivity for other gases were obtained as follows. In the following formulae, (HFC-134a) and (HFO-1123) respectively represent the area ratios (%) of (HFC-134a) and (HFO-1123) in the outlet gas.

[0105] The results are shown in the lower rows in Table 14 with respect to Examples 1 and 2 and in the lower rows in Table 15 with respect to Comparative Examples 1 and 2.

[Degree of conversion (%) of HFC-134a]

[0106] It represents the proportion of components other than HFC-134a among components derived from HFC-134a in the outlet gas. It is calculated from {100-(HFC-134a)}/100 × 100 (%) in the outlet gas.

[Selectivity (%) for HFO-1123]

[0107] It represents the proportion of HFC-134a converted to HFO-1123 based on the entire HFC-134a reacted, represented by %. It is calculated from (HFO-1123)/{100-(HFC-134a)} × 100 (%) in the outlet gas.

[Selectivity (%) for other gases]

[0108] It represents the proportion of HFC-134a converted to compounds other than HFO-1123 based on the entire HFC-134a reacted, represented by %. It is calculated from {100-(HFC-134a)-(HFO-1123)}/{100-(HFC-134a)} ×100 (%) in the outlet gas.

[Table 14]

		Example 1	Example 2
Solid reactant		Potassium carbonate FG	
Reactant packing amount (g)		55	
Reactant packing amount (mmol)		398	
Nitrogen flow rate before reaction (mmol/min)		50.3	46.6
Reaction temperature (°C)		360	410
HFC-134a flow rate at the time of reaction (mmol/min)		2.5	2.3
Nitrogen flow rate at the time of reaction (mmol/min)		50.3	46.6
Composition ratio at the time of reaction HFC-134a : N2 (molar ratio)		5:95	5:95
Linear velocity at the time of reaction (cm/s)		12.0	12.0
Compact time at the time of reaction (s)		1.25	1.25
Fluidized state at the time of reaction		Completely fluidized state	
Reaction time (min)		10	10
Structure	Name	Outlet gas composition (other than nitrogen) (area%)	
CF2=CHF	HFO-1123	3.8	4.2
CF3CH2F	HFC-134a	96.0	95.6
Others		0.2	0.2
Degree of conversion of HFC-134a (%)		4.0	4.4
Selectivity for HFO-1123 (%)		95.1	95.6
Selectivity for other gases (%)		4.9	4.4

[Table 15]

	Comparative Example 1	Comparative Example 2
Solid reactant	Potassium carbonate FG R-10	
Reactant packing amount (g)	18	
Reactant packing amount (mmol)	127	
Nitrogen flow rate before reaction (mmol/min)	6.24	5.78
Reaction temperature (°C)	360	410
HFC-134a flow rate at the time of reaction (mmol/min)	0.31	0.29
Nitrogen flow rate at the time of reaction (mmol/min)	6.24	5.78

(continued)

		Comparative Example 1	Comparative Example 2
Composition ratio at the time of reaction HFC-134a : N2 (molar ratio)		5:95	5:95
Linear velocity at the time of reaction (cm/s)		1.5	1.5
Compact time at the time of reaction (s)		10.00	10.00
Fluidized state at the time of reaction		No fluidization	
Reaction time (min)		15	15
Structure	Name	Outlet gas composition (other than nitrogen) (area%)	
CF2=CHF	HFO-1123	5.0	5.8
CF3CH2F	HFC-134a	93.5	93.7
Others		1.5	0.5
Degree of conversion of HFC-134a (%)		6.5	6.3
Selectivity for HFO-1123 (%)		76.4	91.6
Selectivity for other gases (%)		23.6	8.4

B. Synthesis reaction using calcium oxide as solid reactant

(Analysis conditions)

[0109] The composition of the outlet gas was analyzed under the same conditions as in Example 1.

(Reaction apparatus 2)

[0110] As a reaction apparatus 2, a fluidized bed reaction apparatus 16 shown in Fig. 16 was used. The fluidized bed reaction apparatus 16 shown in Fig. 16 comprises the fluidized bed reaction apparatus 1 shown in Fig. 1, provided with a differential pressure measuring device to measure a differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor 2.

[0111] In the fluidized bed reaction apparatus 16, as the fluidized bed reactor 2, a reactor for a vertical fluidized bed having an inner diameter of 106.3 mm and a height of 550 mm made of stainless steel (SUS316) was used, a SUS316 insertion tube having a diameter of 6 mm was introduced in the vertical direction of the reactor, a type K thermocouple was inserted to the insertion tube, and the temperature in the reactor was measured. Further, a grating was disposed at the lowest portion of the fluidized bed reactor 2, and a solid reactant was packed thereon to form a solid reactant layer 3. The interior of the fluidized bed reactor 2 was heated by an electric heater 2a.

[0112] A preheating mixer 4 was connected to the lower portion of the fluidized bed reactor 2 via a material gas supply line 5. The material gas supply line 5 and the preheating mixer 4 were respectively heated to 200 to 450°C by a ribbon heater. The apparatus was so constituted that HFC-134a and nitrogen as a diluent gas were mixed while their flow rates were adjusted respectively by mass flow controllers 6a and 7a provided to a HFC-134a supply line 6 and a diluent gas supply line 7, and the gas mixture was supplied to the preheating mixer 4 through a gas mixture supply line 12. The outlet gas containing a reaction product was continuously withdrawn from the upper portion of the fluidized bed reactor 2, collected in a sampling bag made of polyvinylidene fluoride (PVdF) (hereinafter referred to as PVdF bag), and subjected to composition analysis by means of gas chromatography (GC).

[0113] Further, the differential pressure measuring device was constituted as follows. That is, a digital differential pressure gauge 17 was disposed between an outlet side piping connected to the lower portion of the fluidized bed reactor 2 and an outlet side piping connected to the upper portion.

(Linear velocity)

[0114] The linear velocity of each of the nitrogen gas, HFC-134a and the gas mixture of nitrogen and HFC-134a was obtained by dividing the flow rate (volume flow rate) per unit time of each gas at the reaction temperature under the

reaction pressure by the cross section area of the fluidized bed reactor 2.

Blank Differential Pressure Measurement Example 1

[0115] The differential pressure when a nitrogen gas was made to flow through the empty fluidized bed reactor 2 before packed with the reactant of the fluidized bed reaction apparatus 16 at a flow rate of 3.92 mol/min (linear velocity of 18 cm/s) at room temperature (25°C) under normal pressure was measured. On that occasion, the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor measured by the differential pressure gauge was 10,900 Pa. Then, the nitrogen gas flow rate was gradually decreased, and the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor was measured by the differential pressure gauge at each flow rate.

Blank Differential Pressure Measurement Example 2

[0116] The differential pressure when HFC-134a was made to flow through the empty fluidized bed reactor 2 before packed with the reactant of the fluidized bed reaction apparatus 16 at a flow rate of 2.61 mol/min (linear velocity of 12 cm/s) at room temperature (25°C) under normal pressure was measured. On that occasion, the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor measured by the differential pressure gauge was 11,500 Pa. Then, the HFC-134a flow rate was gradually decreased, and the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor was measured by the differential pressure gauge at each flow rate.

Blank Differential Pressure Measurement Example 3

[0117] The differential pressure when a nitrogen gas was made to flow through the empty fluidized bed reactor 2 before packed with the reactant of the fluidized bed reaction apparatus 16 at a flow rate of 2.47 mol/min (linear velocity of 18 cm/s) at 200°C under normal pressure was measured. On that occasion, the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor measured by the differential pressure gauge was 11,700 Pa. Then, the nitrogen gas flow rate was gradually decreased, and the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor was measured by the differential pressure gauge at each flow rate.

Blank Differential Pressure Measurement Example 4

[0118] The differential pressure when a nitrogen gas was made to flow through the empty fluidized bed reactor 2 before packed with the reactant of the fluidized bed reaction apparatus 16 at a flow rate of 1.25 mol/min (linear velocity of 11 cm/s) at 300°C under normal pressure was measured. On that occasion, the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor measured by the differential pressure gauge was 6,500 Pa. Then, the nitrogen gas flow rate was gradually decreased, and the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor was measured by the differential pressure gauge at each flow rate.

Reactant Packing Example 5

[0119] The fluidized bed reactor 2 of the fluidized bed reaction apparatus 16 was packed with 2,099 g (37.42 mol) of particulate calcium oxide (average particle size: 100 μm, bulk density: 1.2 g/cm^3, specific surface area: 2.9 m^2/g (hereinafter referred to as calcium oxide)) as a solid reactant to a height of 200 mm.

Reactant Packing Example 6

[0120] The fluidized bed reactor 2 of the fluidized bed reaction apparatus 16 was packed with 3,143 g (56.05 mol) of particulate calcium oxide (average particle size: 100 μm, bulk density: 1.2 g/cm^3, specific surface area: 2.9 m^2/g (hereinafter referred to as calcium oxide)) as a solid reactant to a height of 300 mm.

[0121] In the following Fluidization Examples 8 to 12, the fluidization starting velocity was determined in accordance with the calculated differential pressure obtained by subtracting the blank differential pressure before packing with the reactant from the differential pressure after packing with the reactant (hereinafter referred to as differential pressure after packing) under the same conditions (the temperature, the pressure, the type of the gas, the flow rate). In a graph obtained by plotting the calculated differential pressure relative to the linear velocity of the gas, the inflection point at which the gradient of the graph changes is taken as the starting point of fluidization of the solid reactant layer, and the linear velocity at the inflection point may be taken as the fluidization starting velocity. Further, in a graph having two

inflection points in the differential pressure, the linear velocity at an inflection point on the lower linear velocity side is taken as the partial fluidization starting velocity, and the linear velocity at an inflection point on the higher linear velocity side is taken as the complete fluidization starting velocity.

Fluidization Example 8

[0122] Through the fluidized bed reaction apparatus packed with the solid reactant (calcium oxide having an average particle size of 100 μm) to a height of 200 mm shown in Reactant Packing Example 5, a nitrogen gas was made to flow at a flow rate of 3.05 mol/min (linear velocity of 14 cm/s) at room temperature (25°C) under normal pressure. On that occasion, the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor measured by the differential pressure gauge was 10,900 Pa.

[0123] Then, the nitrogen gas flow rate was gradually decreased, and the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor was measured by the differential pressure gauge at each flow rate. The flow rate of the nitrogen gas, the linear velocity, the differential pressure after packing, and the calculated differential pressure obtained by calculating the difference with the Blank Differential Pressure Measurement Example 1 are shown in Table 16. Further, a graph obtained by plotting the calculated differential pressure relative to the linear velocity of the nitrogen gas is shown in Fig. 17. It can be judged from Table 16 and Fig. 17 that in Fluidization Example 8, the complete fluidization starting velocity of the solid reactant layer is 7 cm/s.

[Table 16]

Fluidization Example 8															
Type of reactant		°C	Calcium oxide												
Reactant packing height		mm	200												
Temperature		°C	25												
Gas composition ratio	HFC-134a	mol%	0												
	Nitrogen	mol%	100												
Flow rate	HFC-134a	mol/min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Nitrogen	mol/min	3.05	2.83	2.61	2.39	2.18	1.96	1.74	1.52	1.31	1.09	0.87	0.65	0.44	0.22
Linear velocity		cm/s	14	13	12	11	10	9	8	7	6	5	4	3	2	1
Differential pressure after packing Pa			10900	10000	9300	8500	7700	6900	6100	5400	4700	3900	3300	2500	1900	1200
Blank differential pressure Pa			8700	7900	7100	6400	5700	5000	4200	3500	2900	2300	1800	1200	800	300
Calculated differential pressure Pa			2200	2100	2200	2100	2000	1900	1900	1900	1800	1600	1500	1300	1100	900
* Blank Differential Pressure Measurement Example 1 was employed.																

Fluidization Example 9

[0124] Through the fluidized bed reaction apparatus packed with the solid reactant (calcium oxide having an average particle size of 100 μm) to a height of 300 mm shown in Reactant Packing Example 6, a nitrogen gas was made to flow at a flow rate of 2.83 mol/min (linear velocity of 13 cm/s) at room temperature (25°C) under normal pressure. On that occasion, the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor measured by the differential pressure gauge was 10,200 Pa.

[0125] Then, the nitrogen gas flow rate was gradually decreased, and the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor was measured by the differential pressure gauge at each flow rate. The flow rate of the nitrogen gas, the linear velocity, the differential pressure after packing, and the calculated differential pressure obtained by calculating the difference with the Blank Differential Pressure Measurement Example 1 are shown in Table 17. Further, a graph obtained by plotting the calculated differential pressure relative to the linear velocity of the nitrogen gas is shown in Fig. 18. It can be judged from Table 17 and Fig. 18 that in Fluidization Example 9, the complete fluidization starting velocity of the solid reactant layer is 5 cm/s.

[Table 17]

			Fluidization Example 9												
Type of reactant		°C	Calcium oxide												
Reactant packing height		mm	300												
Temperature		°C	25												
Gas composition ratio	HFC-134a	mol%	0												
	Nitrogen	mol%	100												
Flow rate	HFC-134a	mol/min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Nitrogen	mol/min	2.83	2.61	2.39	2.18	1.96	1.74	1.52	1.31	1.09	0.87	0.65	0.44	0.22
Linear velocity		cm/s	13	12	11	10	9	8	7	6	5	4	3	2	1
Differential pressure after packing Pa			10200	9400	8600	7800	7100	6400	5700	5000	4400	3700	3100	2500	1900
Blank differential pressure Pa			7900	7100	6400	5700	5000	4200	3500	2900	2300	1800	1200	800	300
Calculated differential pressure Pa			2300	2300	2200	2100	2100	2200	2200	2100	2100	1900	1900	1700	1600
* Blank Differential Pressure Measurement Example 1 was employed.															

Fluidization Example 10

[0126] Through the fluidized bed reaction apparatus packed with the solid reactant (calcium oxide having an average particle size of 100 μm) to a height of 200 mm shown in Reactant Packing Example 5, HFC-134a was made to flow at a flow rate of 2.61 mol/min (linear velocity of 12 cm/s) at room temperature (25°C) under normal pressure. On that occasion, the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor measured by the differential pressure gauge was 13,400 Pa.

[0127] Then, the HFC-134a flow rate was gradually decreased, and the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor was measured by the differential pressure gauge at each flow rate. The flow rate of HFC-134a, the linear velocity, the differential pressure after packing, and the calculated differential pressure obtained by calculating the difference with the Blank Differential Pressure Measurement Example 2 are shown in Table 18. Further, a graph obtained by plotting the calculated differential pressure relative to the linear velocity of HFC-134a is shown in Fig. 19. It can be judged from Table 18 and Fig. 19 that in Fluidization Example 10, the complete fluidization starting velocity of the solid reactant layer is 6 cm/s.

[Table 18]

Fluidization Example 10												
Type of reactant		°C	Calcium oxide									
Reactant packing height		mm	200									
Temperature		°C	25									
Gas composition ratio	HFC-134a	mol%	100									
	Nitrogen	mol%	0									
Flow rate	HFC-134a	mol/min	2.61	2.39	2.18	1.96	1.74	1.52	1.31	1.09	0.87	0.65	0.44	0.22
	Nitrogen	mol/min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Linear velocity		cm/s	12	11	10	9	8	7	6	5	4	3	2	1
Differential pressure after packing		Pa	13400	12200	10900	9600	8400	7200	6200	5000	3900	2900	2000	1300
Blank differential pressure		Pa	11500	10300	9000	7800	6700	5400	4400	3400	2300	1500	900	300
Calculated differential pressure		Pa	1900	1900	1900	1800	1700	1800	1800	1600	1600	1400	1100	1000
* Blank Differential Pressure Measurement Example 2 was employed.														

Fluidization Example 11

[0128] Through the fluidized bed reaction apparatus packed with the solid reactant (calcium oxide having an average particle size of 100 μm) to a height of 200 mm shown in Reactant Packing Example 5, a nitrogen gas was made to flow at a flow rate of 2.19 mol/min (linear velocity of 16 cm/s) at 200°C under normal pressure. On that occasion, the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor measured by the differential pressure gauge was 1,200 Pa.

[0129] Then, the nitrogen gas flow rate was gradually decreased, and the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor was measured by the differential pressure gauge at each flow rate. The flow rate of the nitrogen gas, the linear velocity, the differential pressure after packing, and the calculated differential pressure obtained by calculating the difference with the Blank Differential Pressure Measurement Example 3 are shown in Table 19. Further, a graph obtained by plotting the calculated differential pressure relative to the linear velocity of the nitrogen gas is shown in Fig. 20. It can be judged from Table 19 and Fig. 20 that in Fluidization Example 11, the complete fluidization starting velocity of the solid reactant layer is 3 cm/s.

[Table 19]

			Fluidization Example 11							
Type of reactant		°C	Calcium oxide							
Reactant packing height		mm	200							
Temperature		°C	200							
Gas composition ratio	HFC-134a	mol%	0							
	Nitrogen	mol%	100							
Flow rate	HFC-134a	mol/min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Nitrogen	mol/min	2.19	2.06	1.92	1.78	1.65	1.51	1.37	1.23
Linear velocity		cm/s	16	15	14	13	12	11	10	9
Differential pressure after packing		Pa	11200	10500	9800	9100	8500	7700	7000	6300
Blank differential pressure		Pa	10100	9500	8800	8100	7300	6600	5900	5100
Calculated differential pressure		Pa	1100	1000	1000	1000	1200	1100	1100	1200

* Blank Differential Pressure Measurement Example 3 was employed.

[Table 19] (continued)

			Fluidization Example 11							
Type of reactant		°C	Calcium oxide							
Reactant packing height		mm	200							
Temperature		°C	200							
Gas composition ratio	HFC-134a	mol%	0							
	Nitrogen	mol%	100							
Flow rate	HFC-134a	mol/min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Nitrogen	mol/min	1.10	0.96	0.82	0.69	0.55	0.41	0.27	0.14
Linear velocity		cm/s	8	7	6	5	4	3	2	1
Differential pressure after packing		Pa	5600	4900	4300	3700	3100	2400	1900	1200
Blank differential pressure		Pa	4500	3800	3200	2600	2000	1400	900	400
Calculated differential pressure		Pa	1100	1100	1100	1100	1100	1000	1000	800

* Blank Differential Pressure Measurement Example 3 was employed.

Fluidization Example 12

[0130] Through the fluidized bed reaction apparatus packed with the solid reactant (calcium oxide having an average particle size of 100 μm) to a height of 200 mm shown in Reactant Packing Example 5, a nitrogen gas was made to flow at a flow rate of 1.25 mol/min (linear velocity of 11 cm/s) at 300°C under normal pressure. On that occasion, the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor measured by the differential pressure gauge was 7,700 Pa.

[0131] Then, the nitrogen gas flow rate was gradually decreased, and the differential pressure between on the inlet side and on the outlet side of the fluidized bed reactor was measured by the differential pressure gauge at each flow rate. The flow rate of the nitrogen gas, the linear velocity, the differential pressure after packing, and the calculated differential pressure obtained by calculating the difference with the Blank Differential pressure Measurement Example 4 are shown in Table 20. Further, a graph obtained by plotting the calculated differential pressure relative to the linear velocity of the nitrogen gas is shown in Fig. 21. It can be judged from Table 20 and Fig. 21 that in Fluidization Example 12, the complete fluidization starting velocity of the solid reactant layer is 3 cm/s.

[Table 20]

Fluidization Example 12												
Type of reactant		°C	Calcium oxide									
Reactant packing height		mm	200									
Temperature		°C	300									
Gas composition ratio	HFC-134a	mol%	0									
	Nitrogen	mol%	100									
Flow rate	HFC-134a	mol/min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Nitrogen	mol/min	1.25	1.13	1.02	0.91	0.79	0.68	0.57	0.45	0.34	0.23	0.11
Linear velocity		cm/s	11	10	9	8	7	6	5	4	3	2	1
Differential pressure after packing		Pa	7700	7000	6300	5700	5000	4300	3700	3100	2500	1900	1200
Blank differential pressure		Pa	6500	5900	5100	4500	3800	3200	2600	2000	1500	900	400
Calculated differential pressure		Pa	1200	1100	1200	1200	1200	1100	1100	1100	1000	1000	800
* Blank Differential Pressure Measurement Example 4 was employed.													

[0132] The results of the fluidization tests in the above Fluidization Examples 8 to 12 are shown in Table 21. It is found from Table 21 that calcium oxide having an average particle size of 100 μm has favorable flowability, and it can be in a fluidized state by making a gas to flow therethrough at a linear velocity of at least 7 cm/s regardless of the type of the gas and the packing height. Further, it is found that the flowability increases as the temperature increases.

[Table 21]

		Fluidization Example 8	Fluidization Example 9	Fluidization Example 10	Fluidization Example 11	Fluidization Example 12
Reactant Packing Example		Packing Example 5	Packing Example 6	Packing Example 5	Packing Example 5	Packing Example 5
Average particle size of calcium oxide μm		100	100	100	100	100
Fluidization visualized test apparatus or fluidized bed reaction apparatus		Fluidized bed reaction apparatus	Fluidized bed reaction apparatus	Fluidized bed reaction apparatus	Fluidized bed reaction apparatus	Fluidized bed reaction apparatus
Temperature °C		25	25	25	200	300
Gas composition ratio	HFC-134a mol%	0	0	100	0	0
	Nitrogen mol%	100	100	0	100	100
Linear velocity/ differential pressure plot analysis	Partial fluidization starting velocity	Nil	Nil	Nil	Nil	Nil
	Complete fluidization starting velocity	7 cm/s	5 cm/s	6 cm/s	3 cm/s	3 cm/s

Examples 3 to 10

[0133] First, in Example 3, the interior of the fluidized bed reactor of the fluidized bed reaction apparatus packed with the solid reactant (calcium oxide having an average particle size of 100 μm) to a height of 300 mm shown in Reactant Packing Example 6 was heated to 300°C by an electric furnace. Then, a nitrogen gas was made to flow through the fluidized bed reaction apparatus at a flow rate of 0.79 mol/min (linear velocity of 7 cm/s) under normal pressure. From the results of the above Fluidization Examples 8 to 12, it is considered that the layer of calcium oxide was in a completely fluidized state at this linear velocity.

[0134] Then, the flow rate of the nitrogen gas was decreased to 0.71 mol/min and at the same time, HFC-134a was started to be made to flow at a flow of 0.08 mmol/min. HFC-134a was made to flow and reacted for 2 minutes from the start of the flow of HFC-134a, and then the supply of HFC-134a was terminated and at the same time, the flow rate of the nitrogen gas was changed to 0.79 mol/min, and the reaction in Example 3 was completed. The outlet gas for about 10 seconds from 2 minutes after the start of the flow of HFC-134a to the completion of the reaction was continuously collected in a PVdF bag.

[0135] Then, after completion of the reaction in Example 3, without exchanging calcium oxide in the fluidized bed reactor, Examples 4 to 10 were carried out as it was. In Examples 4 to 10, HFC-134a was brought into contact with and reacted with the solid reactant in the same manner as in Example 3 except that the reaction conditions were as identified in Table 22. Further, the composition of the outlet gas collected in the PVdF bag was analyzed by gas chromatography (GC). The analysis results are shown in Table 22 together with the reaction conditions (the nitrogen flow rate before the reaction, the reaction temperature, the HFC-134a flow rate at the time of the reaction, the nitrogen flow rate at the time of the reaction, the composition at the time of the reaction (HFC-134a: nitrogen (molar ratio)), the linear velocity at the time of the reaction, the contact time at the time of the reaction, presence or absence of the fluidized state at the time of the reaction, and the reaction time).

Examples 11 to 15

[0136] First, in Example 1, the interior of the fluidized bed reactor of the fluidized bed reaction apparatus packed with the solid reactant (calcium oxide having an average particle size of 100 μm) to a height of 300 mm shown in Reactant Packing Example 6 was heated to 350°C by an electric furnace. And, a nitrogen gas was made to flow through the fluidized bed reaction apparatus at a flow rate of 0.73 mmol/min (linear velocity of 7 cm/s) under normal pressure. From the results of the above Comparative Fluidization Examples 8 to 12, it is considered that the layer of calcium oxide was in a completely fluidized state at this linear velocity.

[0137] Then, simultaneously with termination of the flow of the nitrogen gas, , HFC-134a was started to be made to flow at a flow rate of 0.73 5 mmol/min. HFC-134a was made to flow and reacted for 3 minutes from the start of the flow of HFC-134a, and only the supply of HFC-134a was terminated and at the same time, the flow rate of the nitrogen gas was changed to 0.73 mol/min, to complete the reaction in Example 11. The outlet gas was continuously collected in a PVdF bag for about 10 seconds from 5 minutes after the start of the flow of HFC-134a to the completion of the reaction.

[0138] Then, after completion of the reaction in Example 11, without exchanging potassium calcium oxide in the fluidized bed reactor, Examples 12 to 15 were conducted as it was. In Examples 12 to 15, HFC-134a was brought into contact with and reacted with the solid reactant in the same manner as in Example 11 except that the reaction conditions were as identified in Table 23. And, the composition of the outlet gas collected in the PVdF bag was analyzed by gas chromatography (GC). The analysis results are shown in Table 23 together with the reaction conditions (the nitrogen flow rate before the reaction, the reaction temperature, the HFC-134a flow rate at the time of the reaction, the nitrogen flow rate at the time of the reaction, the composition at the time of the reaction (HFC-134a: nitrogen (molar ratio)), the linear velocity at the time of the reaction, the contact time at the time of the reaction, presence or absence of the fluidized state at the time of the reaction, and the reaction time).

[0139] Then, in Examples 3 to 10 and 11 to 15, based on the molar ratio (mol%) calculated from the area ratio of the outlet gas obtained by gas chromatography analysis, the degree of conversion (reactivity) of HFC-134a, the selectivity for HFO-1123 and the selectivity for other gases were obtained as follows. In the following reaction formulae, (HFC-134a) and (HFO-1123) respectively represent the molar ratios (mol%) of (HFC-134a) and (HFO-1123) in the outlet gas.

[0140] The results are shown in the lower rows in Table 22 with respect to Examples 3 to 10 and in the lower rows in Table 23 with respect to Examples 11 to 15.

[Degree of conversion (%) of HFC-134a]

[0141] It represents the proportion of components other than HFC-134a among components derived from HFC-134a in the outlet gas. It is calculated from {100-(HFC-134a)}/100 × 100 (%) in the outlet gas.

[Selectivity (%) for HFO-1123]

[0142] It represents the proportion of HFC-134a converted to HFO-1123 based on the entire HFC-134a reacted, represented by %. It is calculated from (HFO-1123)/{100-(HFC-134a)} × 100 (%) in the outlet gas.

[Selectivity (%) for other gases]

[0143] It represents the proportion of HFC-134a converted to compounds other than HFO-1123 based on the entire HFC-134a reacted, represented by %. It is calculated from {100-(HFC-134a)-(HFO-1123)}/{100-(HFC-134a)} ×100 (%) in the outlet gas.

[Table 22]

		Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10
Solid reactant		Calcium oxide							
Reactant packing amount (g)		3143							
Reactant packing amount (mol)		56.05							
Nitrogen flow rate before reaction (mol/min)		0.79	0.76	0.73	0.70	0.67	0.65	0.63	0.61
Reaction temperature (°C)		300	325	350	375	400	425	450	475
HFC-134a flow rate at the time of reaction (mol/min)		0.08	0.08	0.07	0.07	0.07	0.06	0.06	0.06
Nitrogen flow rate at the time of reaction (mol/min)		0.71	0.76	0.66	0.63	0.61	0.59	0.57	0.55
Composition ratio at the time of reaction HFC-134a : N2 (molar ratio)		10:90	10:90	10:90	10:90	10:90	10:90	10:90	10:90
Linear velocity at the time of reaction (cm/s)		7	7	7	7	7	7	7	7
Compact time at the time of reaction (s)		4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3
Fluidized state at the time of reaction		Completely fluidized state							
Reaction time (min)		2	2	2	2	2	2	2	2
Structure	Name	Outlet gas composition (other than nitrogen) (mol%)							
CF2=CHF	HFO-1123	7.64	14.23	21.22	30.91	44.09	55.59	63.57	60.70
CF3CH2F	HFC-134a	92.30	85.71	78.68	68.80	55.07	41.88	29.35	22.86
Others		0.1	0.1	0.1	0.3	0.8	2.5	7.1	16.4
Degree of conversion of HFC-134a (%)		7.7	14.3	21.3	31.2	44.9	58.1	70.6	77.1
Selectivity for HFO-1123 (%)		99.2	99.6	99.5	99.1	98.1	95.6	90.0	78.7
Selectivity for other gases (%)		0.8	0.4	0.5	0.9	1.9	4.4	10.0	21.3

[Table 23]

		Example 11	Example 12	Example 13	Example 14	Example 15
Solid reactant		Calcium oxide				
Reactant packing amount (g)		3143				
Reactant packing amount (mol)		56.05				
Nitrogen flow rate before reaction (mol/min)		0.73	0.70	0.67	0.65	0.63
Reaction temperature (°C)		350	375	400	425	450
HFC-134a flow rate at the time of reaction (mol/min)		0.73	0.70	0.67	0.65	0.63
Nitrogen flow rate at the time of reaction (mol/min)		0.00	0.00	0.00	0.00	0.00
Composition ratio at the time of reaction HFC-134a : N2 (molar ratio)		100:0	100:0	100:0	100:0	100:0
Linear velocity at the time of reaction (cm/s)		7	7	7	7	7
Compact time at the time of reaction (s)		4.3	4.3	4.3	4.3	4.3
Fluidized state at the time of reaction		Completely fluidized state				
Reaction time (min)		3	3	3	3	3
Structure	Name	Outlet gas composition (other than nitrogen) (mol%)				
CF2=CHF	HFO-1123	4.65	6.60	10.80	17.24	29.81
CF3CH2F	HFC-134a	95.33	93.36	89.11	82.38	68.03
Others		0.0	0.0	0.1	0.4	2.2
Degree of conversion of HFC-134a (%)		4.7	6.6	10.9	17.6	32.0
Selectivity for HFO-1123 (%)		99.5	99.5	99.2	97.9	93.3
Selectivity for other gases (%)		0.5	0.5	0.8	2.1	6.7

[0144] As evident from Tables 14 and 15, the selectivity for HFO-1123 can be improved in Examples 1 and 2 in which HFC-134a was reacted with potassium carbonate in a fluidized state, as compared with Comparative Examples 1 and 2 in which HFC-134a was reacted with potassium carbonate not in a fluidized state. Further, as evident from Tables 21 and 22, HFO-1123 can be obtained with a high reactivity with a sufficiently high selectivity by reacting HFC-134a with calcium oxide in a fluidized state.

INDUSTRIAL APPLICABILITY

[0145] According to the production method of the present invention, HFO-1123 can be efficiently and stably produced from HFC-134a. The production method is useful as an industrial production method since HFC-134a which is an inexpensive material is used.

[0146] The entire disclosure of Japanese Patent Application No. 2014-15962 filed on January 30, 2014 including specification, claims, drawings and summary is incorporated herein by reference in its entirety.

REFERENCE SYMBOLS

[0147] 1, 11, 16: Fluidized bed reaction apparatus, 2: fluidized bed reactor, 3: solid reactant layer, 4: preheating mixer, 5: material gas supply line, 6: HFC-134a supply line, 7: diluent gas supply line, 8: heating means, 9: outlet line, 10: hydrogen fluoride trapping tube, 12: gas mixture supply line, 13: differential pressure gauge, 14: visualized tester, 15: fluidization visualized test apparatus, 17: digital differential pressure gauge.

Claims

1. A method for producing trifluoroethylene, which comprises making a material gas containing 1,1,1,2-tetrafluoroethane to flow through a layer consisting of a particulate solid reactant having an average particle size of from 1 μm to 5,000 μm to bring the solid reactant and 1,1,1,2-tetrafluoroethane into contact with each other in a state where the layer consisting of the solid reactant is fluidized.

2. The method for producing trifluoroethylene according to Claim 1, wherein the solid reactant has an average particle size of from 40 μm to 500 μm.

3. The method for producing trifluoroethylene according to Claim 1 or 2, wherein the velocity of flow of the material gas containing 1,1,1,2-tetrafluoroethane is from 1 cm/s to 1,000 cm/s by the linear velocity.

4. The method for producing trifluoroethylene according to Claim 3, wherein the velocity of flow of the material gas containing 1,1,1,2-tetrafluoroethane is from 1 cm/s to 20 cm/s by the linear velocity.

5. The method for producing trifluoroethylene according to any one of Claims 1 to 4, wherein the solid reactant contains at least one metal compound selected from the group consisting of a metal oxide, a metal hydroxide, a metal carbonate, a metal sulfate and a metal halide.

6. The method for producing trifluoroethylene according to Claim 5, wherein the metal species contained in the metal compound is at least one member selected from the group consisting of an alkali metal, an alkaline earth metal, a group 13 metal and a group 14 metal.

7. The method for producing trifluoroethylene according to any one of Claims 1 to 6, wherein the solid reactant is potassium carbonate and/or calcium oxide.

8. The method for producing trifluoroethylene according to any one of Claims 1 to 7, wherein the temperature at which 1,1,1,2-tetrafluoroethane and the solid reactant are brought into contact with each other is from 100°C to 500°C.

9. The method for producing trifluoroethylene according to Claim 8, wherein the temperature at which 1,1,1,2-tetrafluoroethane and the solid reactant are brought into contact with each other is from 350°C to 500°C.

10. The method for producing trifluoroethylene according to any one of Claims 1 to 9, wherein the pressure of 1,1,1,2-tetrafluoroethane to be brought into contact with the solid reactant is from 0 to 5 MPa by the gauge pressure.

11. The method for producing trifluoroethylene according to any one of Claims 1 to 10, wherein the contact time of 1,1,1,2-tetrafluoroethane and the solid reactant is from 0.1 second to 100 seconds.

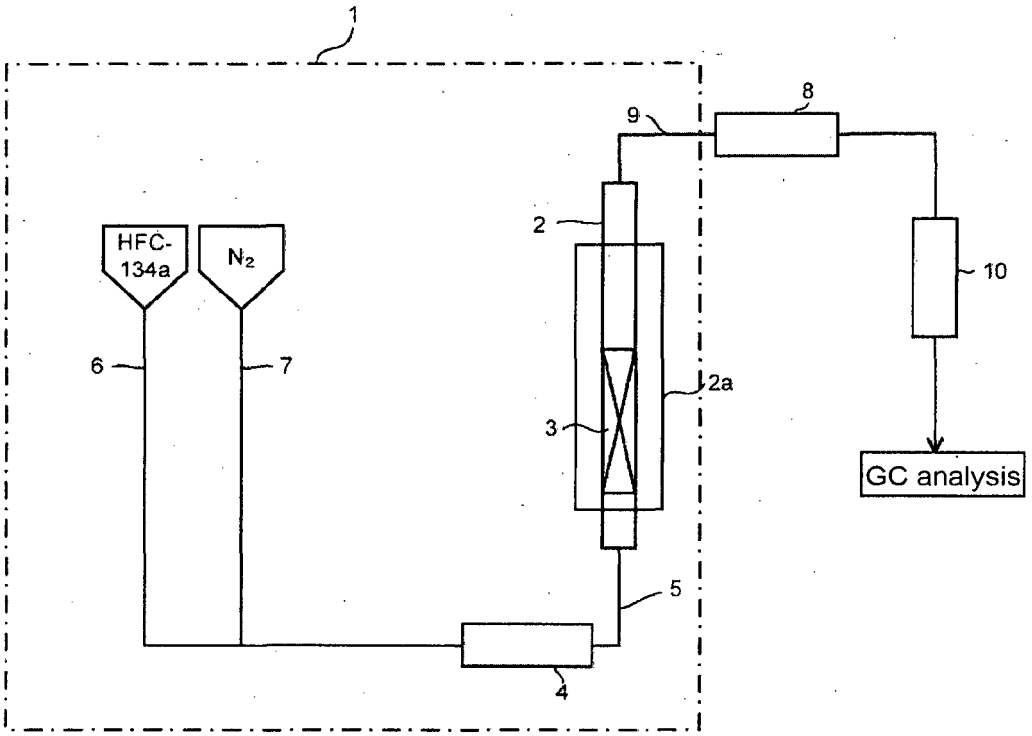
12. The method for producing trifluoroethylene according to Claim 11, wherein the contact time of 1,1,1,2-tetrafluoroethane and the solid reactant is from 0.1 second to 20 seconds.

13. The method for producing trifluoroethylene according to any one of Claims 1 to 12, wherein the content of 1,1,1,2-tetrafluoroethane in the material gas is from 1 mol% to 100 mol%.

14. The method for producing trifluoroethylene according to any one of Claims 1 to 13, wherein the material gas further contains a diluent gas, and its content is at most 95 mol% based on the entire amount of the material gas.

15. The method for producing trifluoroethylene according to any one of Claims 1 to 14, wherein the material gas further contains 1,1,2,2-tetrafluoroethane, and its content is less than 50 mol% based on the total amount of 1,1,1,2-tetrafluoroethane and 1,1,2,2-tetrafluoroethane.

Fig. 1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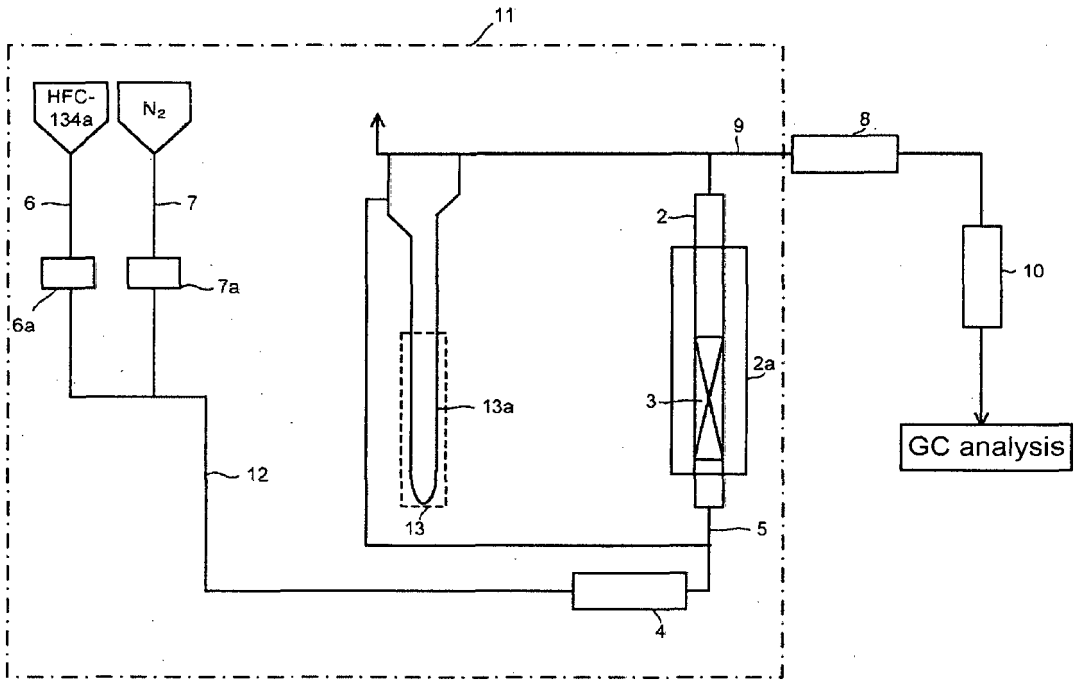
9
2
HFC-134a
N_2
10
6
7
2a
3
GC analysis
5
4

Fig. 2


11
HFC-134a
N_2
9
8
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2
10
7a
6a
2a
13a
3
GC analysis
12
13
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Fig. 3

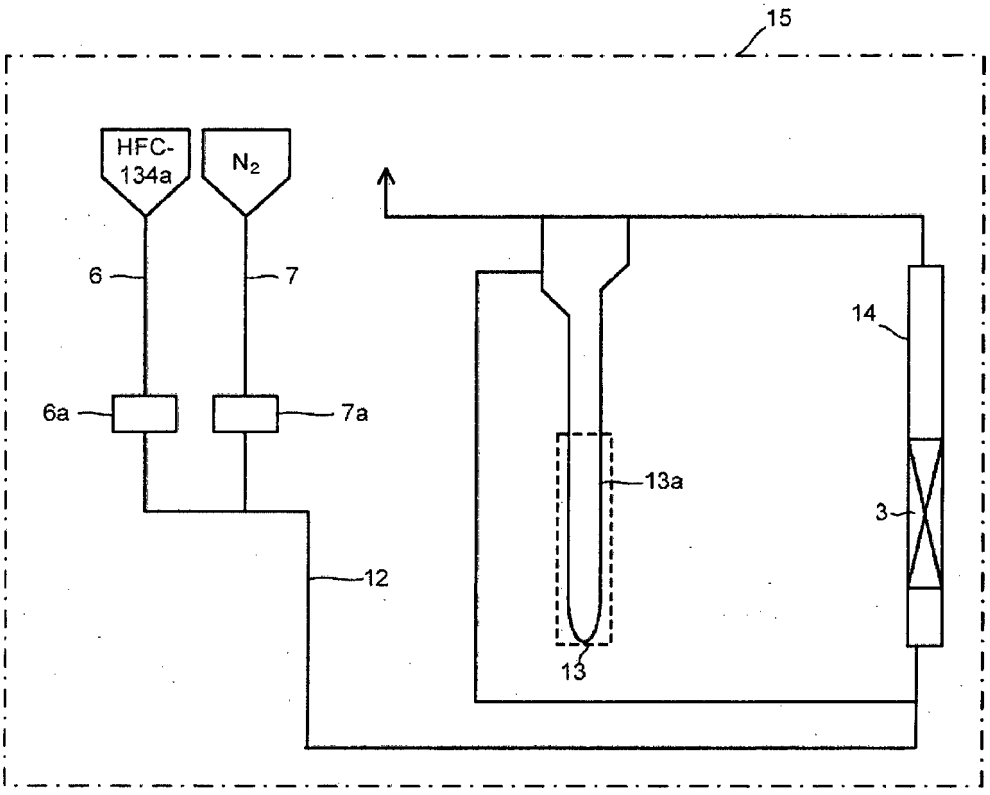


Fig. 4

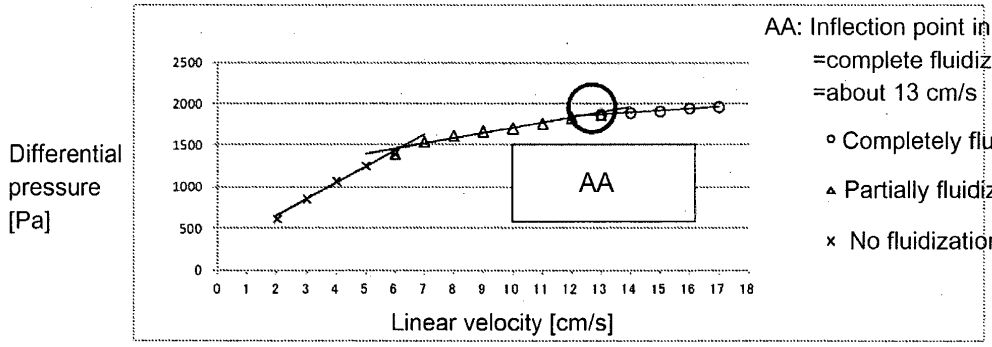

Differential pressure [Pa]
2500
2000
1500
1000
500
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
AA
Linear velocity [cm/s]
AA: Inflection point in data
=complete fluidization starting velocity
=about 13 cm/s
∘ Completely fluidized state
▵ Partially fluidized state
× No fluidization

Fig. 5

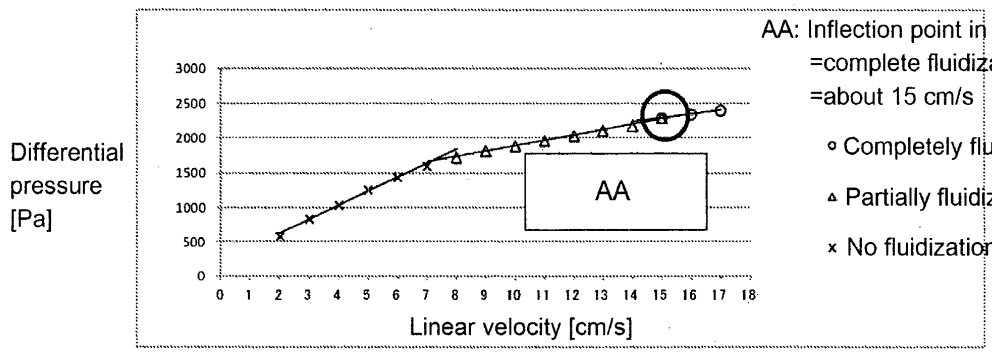

Differential pressure [Pa]
3000
2500
2000
1500
1000
500
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
AA
Linear velocity [cm/s]
AA: Inflection point in data
=complete fluidization starting velocity
=about 15 cm/s
∘ Completely fluidized state
▵ Partially fluidized state
× No fluidization

Fig. 6

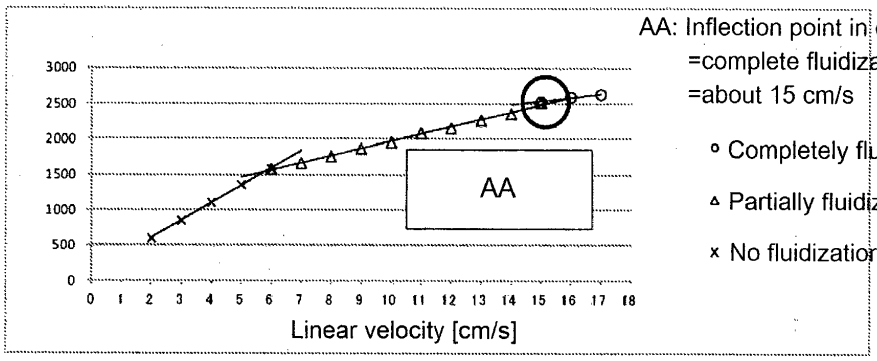

Differential pressure [Pa]
3000
2500
2000
1500
1000
500
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
Linear velocity [cm/s]
AA
AA: Inflection point in data
=complete fluidization starting velocity
=about 15 cm/s
o Completely fluidized state
Δ Partially fluidized state
x No fluidization

Fig. 7

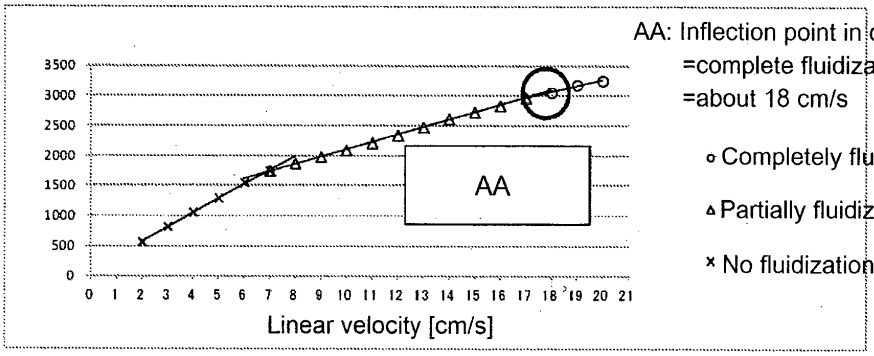

Differential pressure [Pa]
3500
3000
2500
2000
1500
1000
500
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Linear velocity [cm/s]
AA
AA: Inflection point in data
=complete fluidization starting velocity
=about 18 cm/s
o Completely fluidized state
Δ Partially fluidized state
x No fluidization

Fig. 8

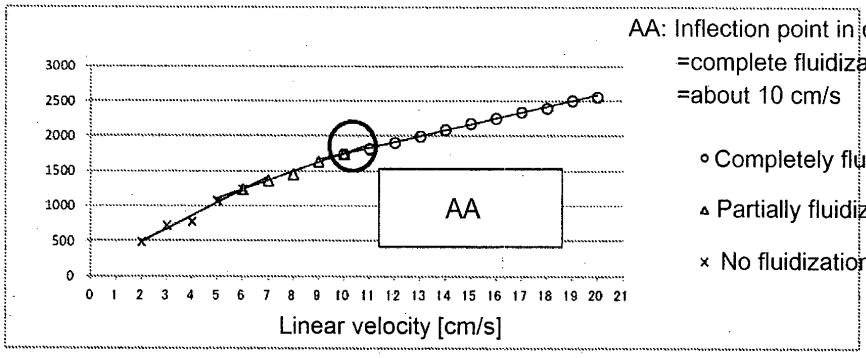

AA: Inflection point in data
=complete fluidization starting velocity
=about 10 cm/s
Differential pressure [Pa]
3000
2500
2000
1500
1000
500
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Linear velocity [cm/s]
AA
∘ Completely fluidized state
▵ Partially fluidized state
× No fluidization

Fig. 9

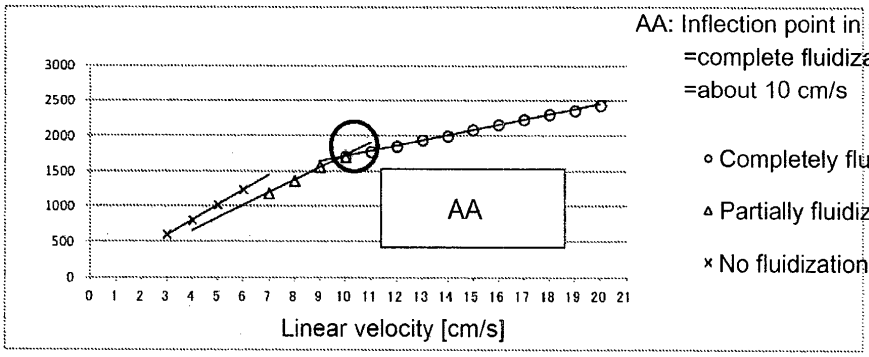

AA: Inflection point in data
=complete fluidization starting velocity
=about 10 cm/s
Differential pressure [Pa]
3000
2500
2000
1500
1000
500
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Linear velocity [cm/s]
AA
∘ Completely fluidized state
▵ Partially fluidized state
× No fluidization

Fig. 10

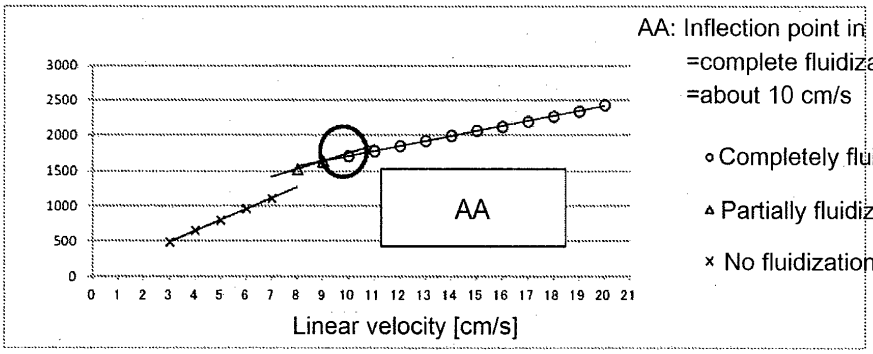

Differential pressure [Pa]
3000
2500
2000
1500
1000
500
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Linear velocity [cm/s]
AA
AA: Inflection point in data
=complete fluidization starting velocity
=about 10 cm/s
Completely fluidized state
Partially fluidized state
No fluidization

Fig. 11

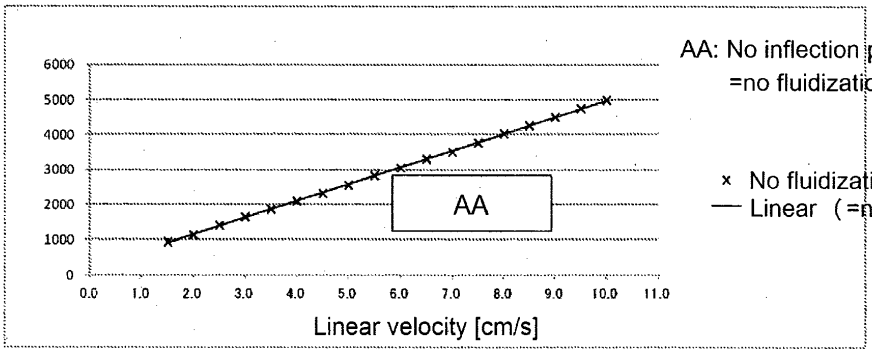

Differential pressure [Pa]
6000
5000
4000
3000
2000
1000
0
0.0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0
Linear velocity [cm/s]
AA
AA: No inflection point in data
=no fluidization observed
No fluidization
Linear (=no fluidization)

Fig. 12

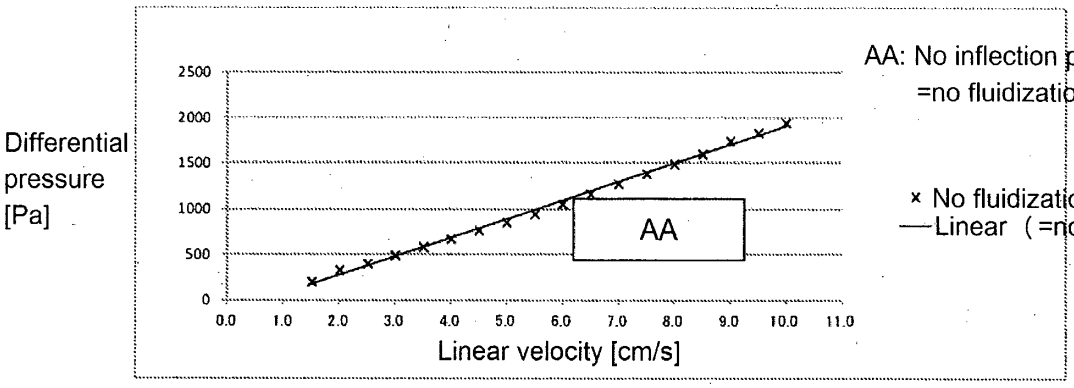

Differential pressure [Pa]
2500
2000
1500
1000
500
0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
AA
Linear velocity [cm/s]
AA: No inflection point in data
=no fluidization observed
× No fluidization
—Linear (=no fluidization)

Fig. 13

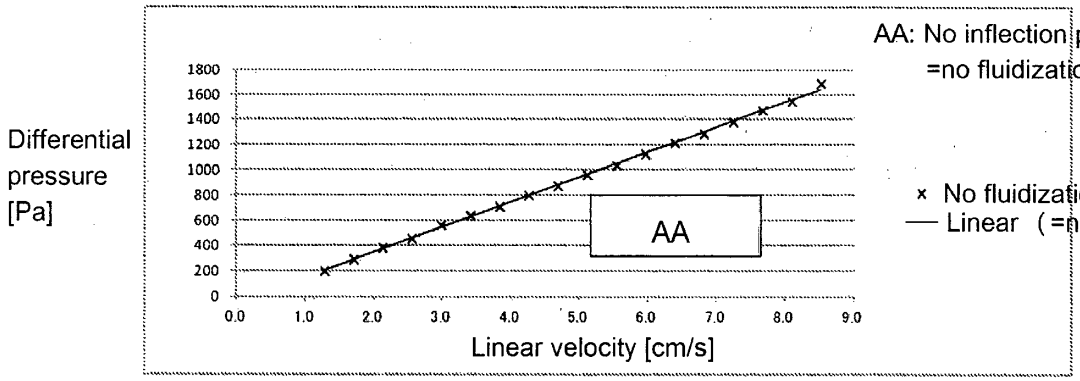

Differential pressure [Pa]
1800
1600
1400
1200
1000
800
600
400
200
0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
AA
Linear velocity [cm/s]
AA: No inflection point in data
=no fluidization observed
× No fluidization
— Linear (=no fluidization)

Fig. 14

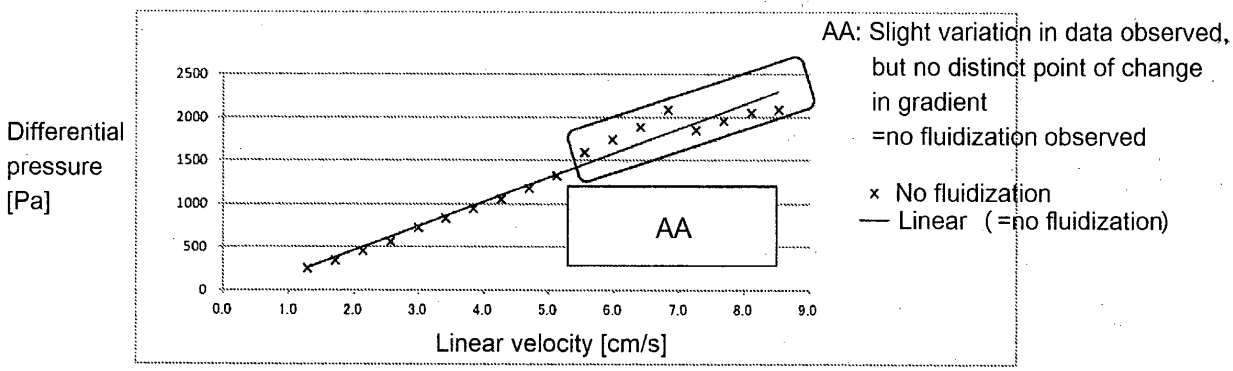

Differential pressure [Pa]
2500
2000
1500
1000
500
0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
AA
Linear velocity [cm/s]
AA: Slight variation in data observed, but no distinct point of change in gradient
=no fluidization observed
× No fluidization
— Linear (=no fluidization)

Fig. 15

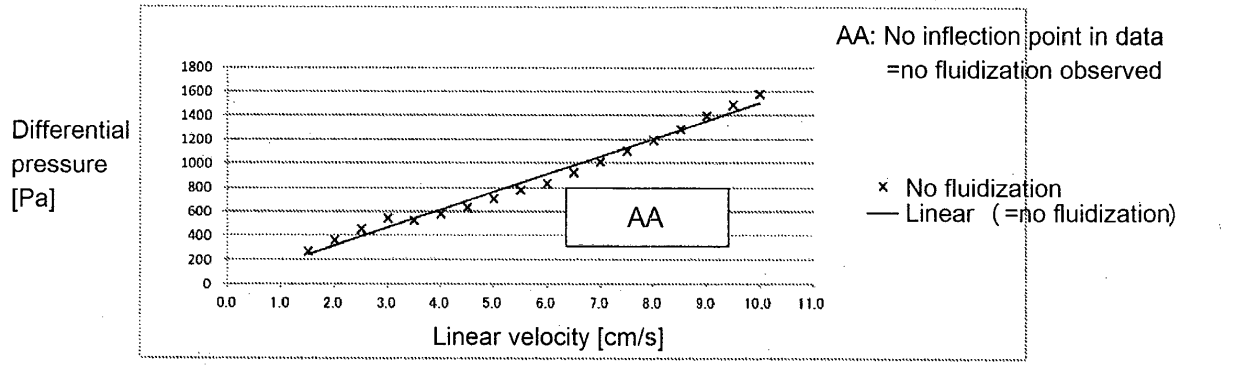

Differential pressure [Pa]
1800
1600
1400
1200
1000
800
600
400
200
0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
AA
Linear velocity [cm/s]
AA: No inflection point in data
=no fluidization observed
× No fluidization
— Linear (=no fluidization)

Fig. 16

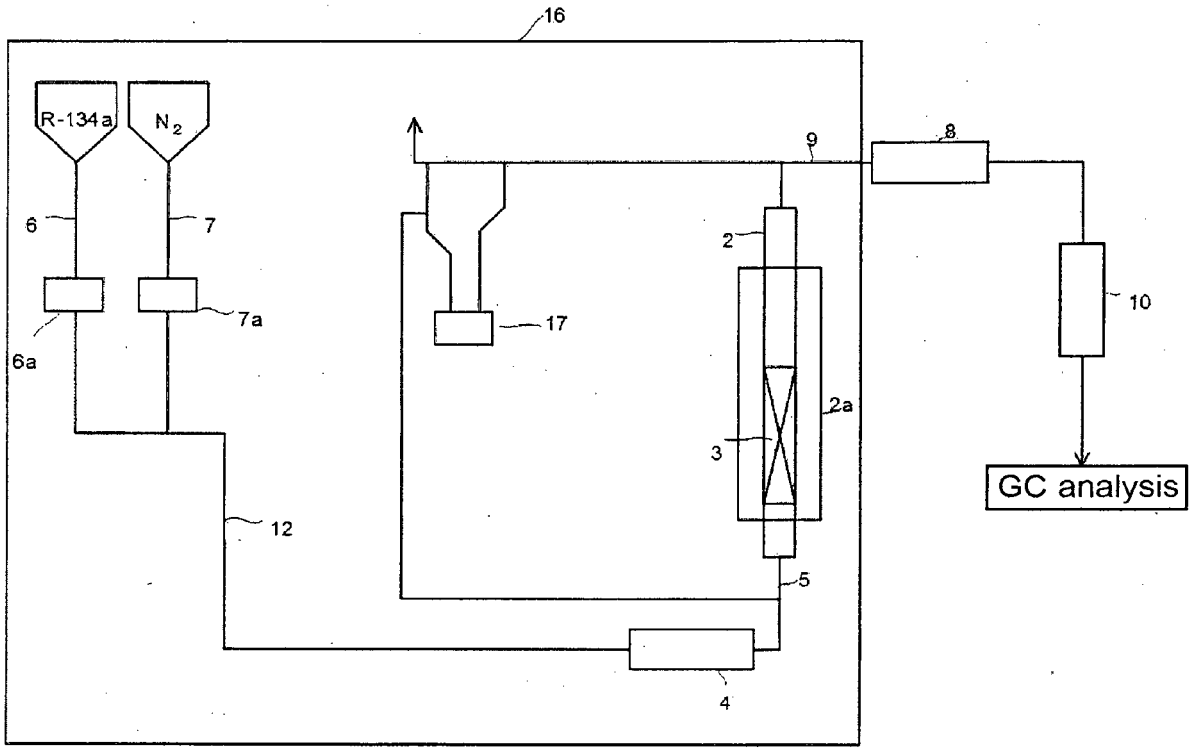

16
R-134a
N_2
6
7
6a
7a
12
17
9
8
2
10
2a
3
5
4
GC analysis

Fig. 17

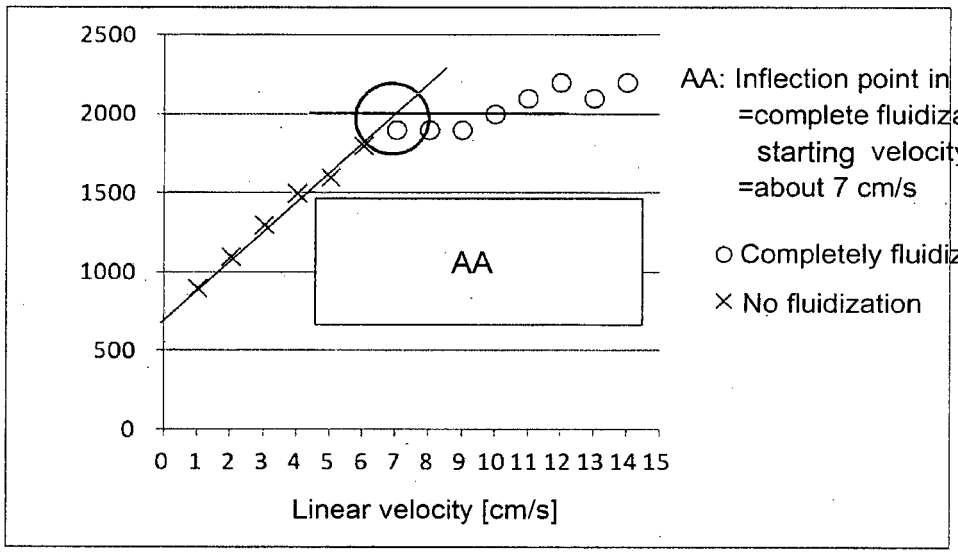

Differential pressure [Pa]
2500
2000
1500
1000
500
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
Linear velocity [cm/s]
AA
AA: Inflection point in data
=complete fluidization starting velocity
=about 7 cm/s
○ Completely fluidized state
× No fluidization

Fig. 18

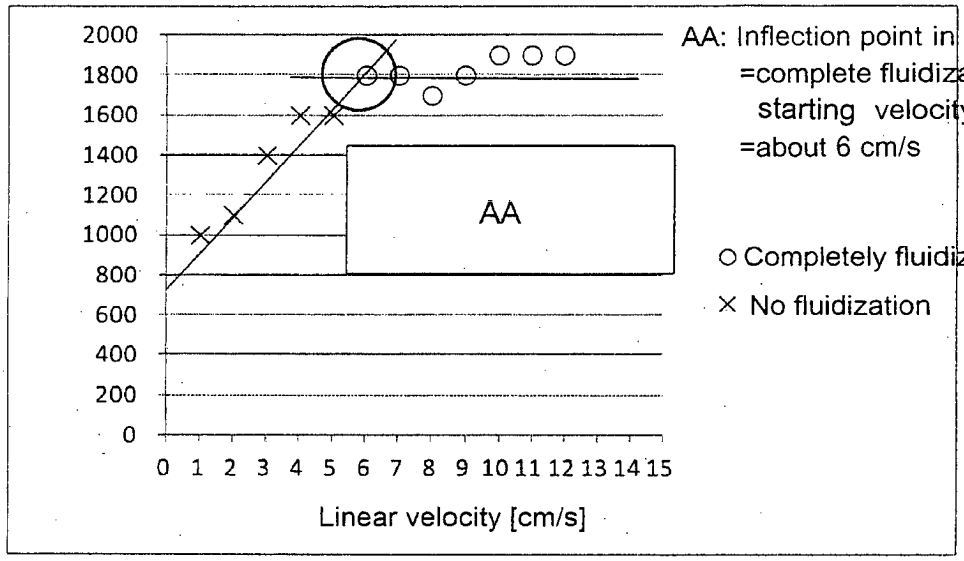

Differential pressure [Pa]
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
Linear velocity [cm/s]
AA
AA: Inflection point in data
=complete fluidization
starting velocity
=about 6 cm/s
○ Completely fluidized state
× No fluidization

Fig. 19

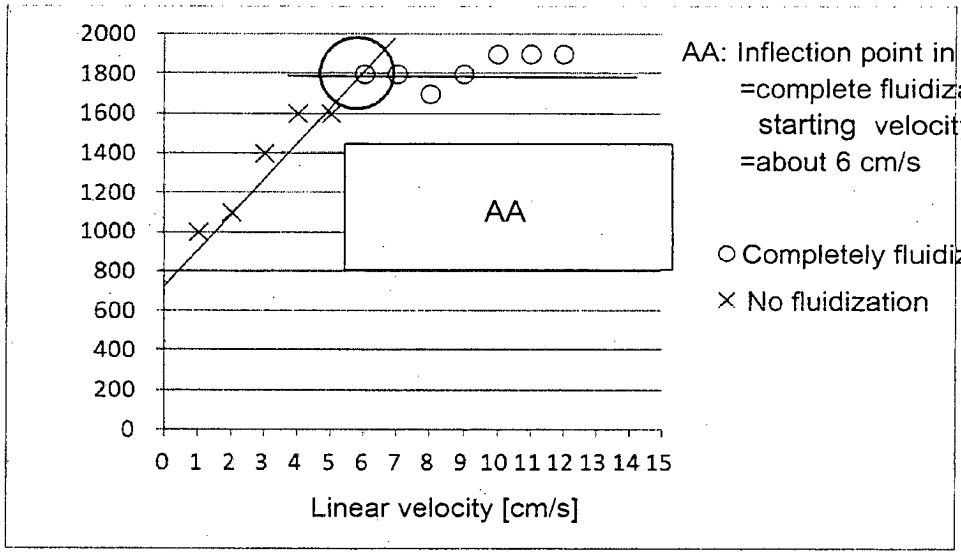

Differential pressure [Pa]
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
Linear velocity [cm/s]
AA
AA: Inflection point in data
=complete fluidization
starting velocity
=about 6 cm/s
○ Completely fluidized state
× No fluidization

Fig. 20

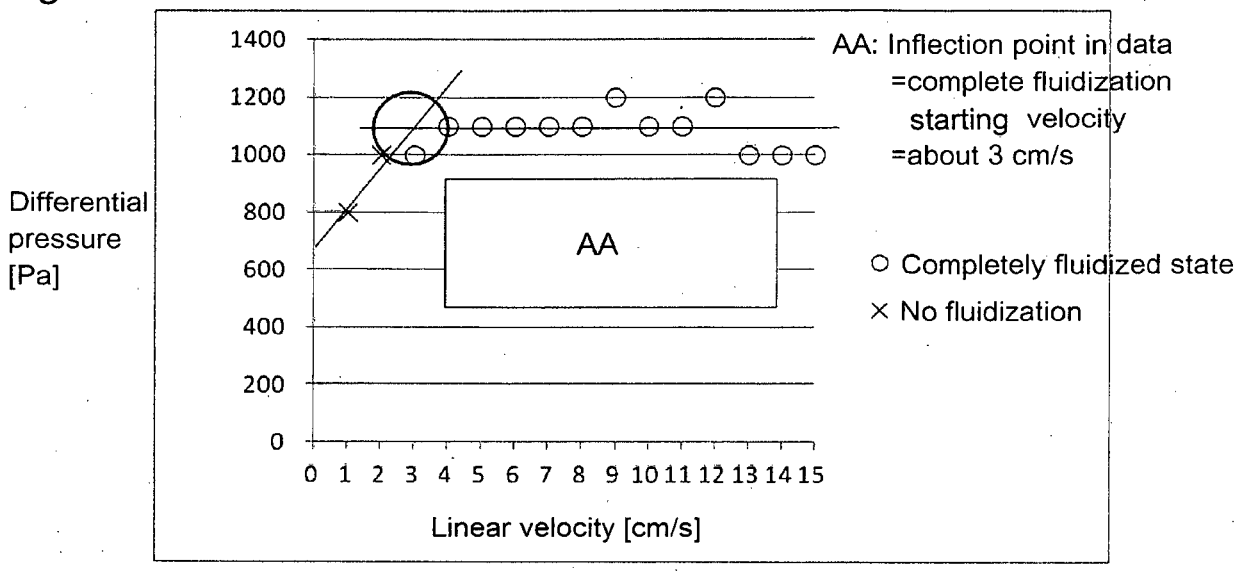
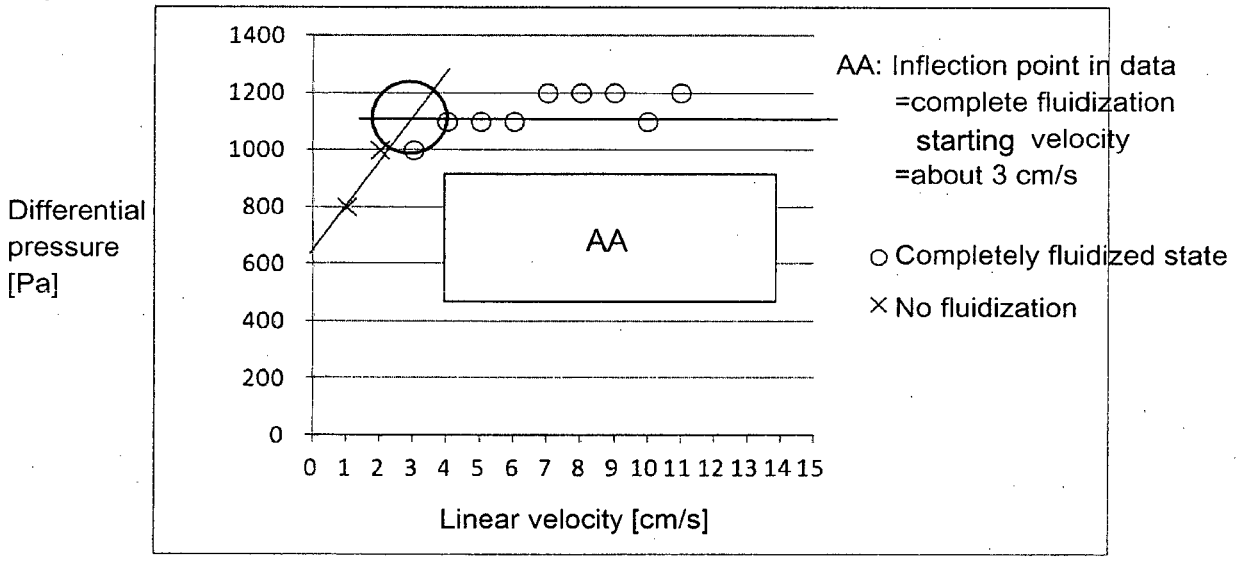

Differential pressure [Pa]
1400
1200
1000
800
600
400
200
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
Linear velocity [cm/s]
AA
AA: Inflection point in data
=complete fluidization
starting velocity
=about 3 cm/s
○ Completely fluidized state
× No fluidization

Fig. 21


Differential pressure [Pa]
1400
1200
1000
800
600
400
200
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
Linear velocity [cm/s]
AA
AA: Inflection point in data
=complete fluidization
starting velocity
=about 3 cm/s
○ Completely fluidized state
× No fluidization

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/052527

A. CLASSIFICATION OF SUBJECT MATTER
C07C17/25(2006.01)i, *C07C21/18*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C17/25, C07C21/18

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2015
Kokai Jitsuyo Shinan Koho 1971-2015 Toroku Jitsuyo Shinan Koho 1994-2015

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
CAplus/REGISTRY(STN), Scopus

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2011/157907 A1 (ARKEMA FRANCE), 22 December 2011 (22.12.2011), pages 6, 7, 9, 10 & FR 2961203 A1	1-6,8-15
Y	JP 10-505337 A (Imperial Chemical Industries PLC), 26 May 1998 (26.05.1998), claims; pages 7 to 8; examples & US 5856593 A & GB 9416009 A & GB 9423778 A & WO 1996/005157 A1 & EP 775100 A & DE 69519379 D & DK 775100 T	1-6,8-15

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
09 April 2015 (09.04.15)	21 April 2015 (21.04.15)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/052527

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Takashi SHIRAI, "Ryudo Shokubai, Ryudoso no Shikenho", Chemical Engineering of Japan, 1963, 27 (5), 378-381, particularly, page 378, '1. Ryushi no Okisa to Gas Ryusoku'	1-6,8-15
Y	JP 5-17425 A (Mitsui Toatsu Chemicals, Inc.), 26 January 1993 (26.01.1993), paragraph [0013] (Family: none)	1-6,8-15
Y	JP 6-56705 A (Exxon Research & Engineering Co.), 01 March 1994 (01.03.1994), paragraph [0013] & EP 577280 A1 & CA 2097219 A1	1-6,8-15
A	JP 2010-070489 A (Unimatec Co., Ltd.), 02 April 2010 (02.04.2010), paragraphs [0015] to [0017] & US 2011/0207904 A1 & WO 2010/032575 A1 & EP 2330093 A1 & CA 2736551 A	1-15
P,X	WO 2014/178353 A1 (Asahi Glass Co., Ltd.), 06 November 2014 (06.11.2014), paragraphs [0040] to [0042] (Family: none)	1-15

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Patent documents cited in the description

- JP 2010533151 A **[0006]**
- WO 2011157907 A **[0006]**
- JP 2014015962 A **[0146]**